HOLOGRAPHIC OPTICAL ELEMENTS RECORDED IN SILVER HALIDE SENSITIZED GELATIN

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ABSTRACT

The objective of this work was to develop holographic optical elements with high quality, which could be applied for display application such as LCDs (liquid crystal displays) and projection displays. Various aspects including the recording materials, processing method and device designs have been examined and evaluated. A new version of the SHSG (silver halide sensitized gelatin) has been introduced, which makes it possible to manufacture both transmission and reflection type of HOEs (holographic optical elements) with high quality and high efficiency. New designs of HOEs processed with the SHSG method have been applied to LCD backlights, colour reflectors and holographic diffusers.

Chapter 1 explains the necessity of the SHSG process and the history of SHSG processing. Chapter 2 describes the SHSG process which can be applied to transmission HOEs. In this chapter, the materials used for the recording and processing of SHSG method have been investigated and several aspects such as bleaching, hardening and drying methods were examined and evaluated. The outline of Chapter 3 is almost same as Chapter 2 but the investigations in Chapter 3 have been focused on the SHSG process for reflection HOEs, which is more complicated. New transmission and reflection SHSG processing schemes have been found and good results have been achieved. Chapter 4 looks at the possibility of recording colour HOEs using the SHSG process described in Chapter 3.

From Chapter 5 to Chapter 7, the applications of HOEs processed by the SHSG method are described. Chapter 5 takes look at the feasibility of replication of diffusers using SHSG processing method. The replicated diffusers with different structures to conventional ones have high quality in terms of transmittance and diffusing angle. Chapter 6 reviews the problems in the edge-lit recording method and proposes new approaches to record a HOE at an extreme angle. In Chapter 7, HOEs for the field of display applications such as holographic reflectors for reflective LCDs, and extreme angle recorded HOE for LCD backlights are mentioned in detail. Several apparatuses, which were designed and constructed for the manufacturing of HOEs, are introduced with some schematic diagrams.

Successive developments for the application of works introduced herein are undergoing at Samsung, Advanced Institute of Technology, Korea and Centre for Modern Optics, De Montfort University. Further results will be published in due course.

This work has produced 4 conference proceeding papers and 2-refereed papers. One of those papers has appeared at the cover of Applied Optics, Information Processing (Volume 41, number 8, 10 March 2002), and 3 patents have been applied for by the sponsor of this work, Samsung Electronics Co.

Publications:

1. **J. M. Kim**, H. I. Bjelkhagen and N. J. Phillips, "HOEs recorded in silver halide sensitized gelatin emulsions", in Practical Holography XIV and Holographic Materials VI, S. A. Benton, S. H. Stevenson and T. J. Trout, eds. Proc. SPIE **3956**, pp. 354-366 (2000).
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3. **J. M. Kim**, B. S. Choi, S. I. Kim, H. I. Bjelkhagen, and N. J. Phillips, "A holographic optical elements recorded in silver halide sensitized gelatin emulsions. Part 1. Transmission holographic optical elements", Appl. Opt. Vol. **40**, pp. 622-632 (2001).
4. **J. M. Kim**, B. S. Choi, Y. S. Choi, J. M. Kim, H. I. Bjelkhagen, and N. J. Phillips, "A holographic optical elements recorded in silver halide sensitized gelatin emulsions. Part 2. Reflection holographic optical elements", Appl. Opt. Vol. **41**, pp. 1522-1533 (2002).
5. **J. M. Kim**, Y. S. Choi, H. I. Bjelkhagen and N. J. Phillips, "SHSG processing for three-wavelength HOEs recording in silver halide materials", in Practical Holography XVI and Holographic Materials VI, S. A. Benton, S. H. Stevenson and T. J. Trout, eds. Proc. SPIE **4659**, pp. 378-387 (2002).
6. K. S. Choi, B. S. Choi, Y. S. Choi, S. I. Kim, **J. M. Kim** et al., " Multiphase computer-generated holograms for full-color image generation", in Practical Holography XVI and Holographic Materials VI, S. A. Benton, S. H. Stevenson and T. J. Trout, eds. Proc. SPIE **4659**, pp. 242-249 (2002).

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CONTENTS

Chapter 1

Introduction and Background

1.1 Background

Recently, the advancements of multimedia and Internet technology has given rise to the expansion of market size and the field of application in electronic systems, particularly in display systems such as flat panel displays and projection displays. Such a huge transition in the market-demand has led to the development of new devices or systems, which have higher quality than ever before. The trends of development of display systems have been inclined toward miniaturization, low power consumption, and higher performance including brightness, higher resolution and full colour representation. Especially, the compactness, brightness and low power consumption become the most important features in the mobile application. Among the features, the brightness and power consumption are related to the efficiency of light used in the display system. The light emitting efficiencies of existing FPDs (flat panel displays) and projection displays are no higher than 10% when comparisons are made with the input electrical power. This is an important limitation for the current generation of display devices.

In spite of extensive efforts, the required features are very hard to achieve because of the limitations of conventional optical devices. Using traditional optics such as lenses, mirrors and filters, many optical elements need to be relatively arranged to obtain proper lighting for the specific display systems. As the number of optical elements increases, the production cost and the size of system may be increased, and the optical efficiency decreases because of the optical losses. That is the reason why new types of optical elements are indispensable for the development of novel display systems. HOEs (holographic optical elements) are one of the promising candidates for the alternative to usual optics. [1.1]

A HOE is a kind of diffractive optical elements, which can act as multi-functional optical element. The advantages and application will be discussed in detail in Chapter 5, 6 and 7. In order to produce HOEs with high quality, the key issue is which recording material to be employed and how to record in those materials. The characteristics of high resolution, reliability, spectral sensitivity, selectivity and efficiency are required in holographic recording materials since they are regarded as essential properties which can affect the global quality of optical systems. There are various materials such as photoresist, photopolymer, AgHal (silver halide) emulsion, SHSG (silver halide sensitized gelatin) and dichromated gelatin, which can be used for holographic recording. [1.2-5] The typical characteristics of the selected recording materials are listed in Table 1. Some of them have been used widely for several decades but sometimes the overall performance is not still good enough to satisfy the demands of holographers.

Among the recording materials, holographic AgHal emulsions are most popular because of their high sensitivity, high resolving power and panchromatic behavior. AgHal emulsions are used in the form where AgHal grains are dispersed in the gelatin. The grain size directly influences on the resolving power, which lies between 10 nm and 100 nm [1.6, 7, 8] and often differs from emulsion to emulsion according to the manufacturer. Sometimes sensitizing dyes are added to the emulsion to improve the sensitivity at a specific wavelength. After the holographic recording, exposed AgHal grains are developed chemically converting AgHal grains into a silver image. The developing process produces an amplitude hologram that can be transformed into a phase hologram by applying a bleaching process.

Bleaching is an oxidation process, which converts silver atoms into transparent silver compound, that is, rehalogenized AgHal grains. Because silver atoms are very stable in aqueous solution, an oxidizing process is necessary to interact with them. After bleaching, the amplitude hologram turns into a phase hologram. The refractive index modulation arises from the refractive index difference between rehalogenized AgHal grains and gelatin or unexposed remaining AgHal grains in the emulsion.

The DE (diffraction efficiency) of bleached AgHal holograms can be quite high, but they are limited by, e. g. scattering of diffracted light by rehalogenized AgHal grains (normally bigger than original AgHal grains), the variation of emulsion thickness due to the exchange of materials in the emulsion during the process, absorption and staining caused by chemical reaction at the developing and bleaching bath, etc. Although AgHal emulsions seem to be very attractive owing to the advantages mentioned above, the characteristics such as efficiency, scattering, absorption and signal-to-noise ratio are not sufficient for HOEs applicable to precision optics or modern display devices. Additionally, when bleached holograms are exposed to ambient light, printout may take place, which means that photolytic silver is formed in the emulsion, which stains the gelatin and darkens the hologram. Even though this effect can be reduced by additional treatment, this is an important problem for bleached holograms. [1.9]

DCG (dichromated gelatin) has been regarded as one of the best recording materials since it has high resolving power, low absorption and light scattering. In addition DCG holograms are extremely bright because of high refractive index modulation. [1.10, 11] DCG is a gelatin layer that contains a certain amount of dichromate. During the exposure, local hardening takes place due to cross-linking of gelatin in the bright nodes. The cross linkage between gelatin molecules is induced photochemically by the trivalent chromium ion (Cr^{3+}) derived from hexavalent chromium ion (Cr^{6+}) in the DCG materials.

Development is performed by dissolving away unhardened or unreacted chemical compound. Dehydration of processed DCG emulsion is very critical since the refractive index modulation normally occurs in this step and inadequate drying process may destroy the hologram. The most important factors in the dehydration step are environmental conditions (humidity and temperature) and drying speed. A series of solvent baths are used to make sure that no water remains in the final solvent bath. In spite of the explanations of the mechanism for the high refractive index modulation that have been suggested [1.10-14], the mechanism in the formation of the DCG hologram is not fully understood yet. Among possible explanations, Chang and Leonard's theory [1.10] is the most plausible. They claimed that the refractive-index modulation occurs in two phases, the rearrangement of gelatin chains caused by cross-linking and the formation of microvoids formed in selected areas. The initial hardness of emulsion is also one of the most critical factors, which can affect the quality of the hologram since the chemical reaction rate in the emulsion during exposure and processing is influenced by the hardness of emulsion. Even with its abundant advantages, the fields of application of DCG are restricted because DCG emulsion has a low peak sensitivity and poor spectral sensitivity. Especially the exposure energy is about up to 100 times higher than that of AgHal materials (Table 1.1).

The necessity for a new scheme for holographic recording material has arisen from the efforts for overcoming the drawbacks of existing recording materials. Photopolymer has attained some success having panchromatic sensitivity and dry-process capability, but it has also some negative aspects [1.15] such as inconvenience of handling, degradation and short shelf life. To make a breakthrough in the field of holographic recording materials, the necessary characteristics of a processed hologram are more or less similar to those of DCG: but we must improve the energetic and spectral sensitivity of the emulsion. This is an important issue for holographic recording materials. The only one material that meets these demands is SHSG emulsion.

The SHSG (silver halide sensitized gelatin) holograms are similar to holograms recorded in dichromated gelatin, the main recording material for HOEs, but still have the speed advantages of AgHal materials. AgHal materials can be processed in such a way that the final HOEs will have properties like a DCG recorded HOE. Recently, this technique has become more interesting after the introduction of new ultra-high-resolution AgHal emulsions. [1.6, 7, 8] The history of the SHSG process will be discussed in the next section.

The technique of generating an SHSG hologram is to expose a silver halide emulsion and then process it in such a way that local tanning near the silver sites will occur within the emulsion. The tanning action is regarded as a hardening process such as crosslinking of gelatin.

There are two different bleaching techniques which can be applied to SHSG processing. After the emulsion has been developed, it can be bleached with a solvent (reversal) bleach, which means that the developed silver is dissolved. (Fig. 1.1) The other possibility is that the developed silver in the emulsion is rehalogenated using a bleach containing normally potassium bromide. (Fig. 1.2) The two techniques have their advantages and disadvantages and which technique to apply depends on the results one wishes to obtain. For example, to maintain emulsion thickness, the rehalogenating technique is preferred. However, in both processes there is a fixing step applied in which residual materials (silver or AgHal) is removed from the emulsion. If the hardening of the gelatin is not sufficient, shrinkage of the emulsion may occur as a result of the fixing step. However, the selective hardening of the emulsion during bleaching and overall hardening applied to the emulsion during processing may reduce this effect. The last step of the processing is to dehydrate the material using isopropyl alcohol in the same way in which dichromated gelatin holograms are processed. A dry SHSG hologram must be hermetically sealed to prevent moisture penetrating into the emulsion, which would destroy the image. The difference between the SHSG process and the DCG process is that in the DCG process hexavalent chromium is *photolytically* reduced to the trivalent state, while in the SHSG process the same result is arrived at *chemically*. The developed silver in the SHSG emulsion reduces the chromium during bleaching in the rehalogenating dichromate bleach solution:

$$6Ag^0 + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Ag^+ + 2Cr^{3+} + 7H_2O. \qquad (1\text{-}1)$$

In the work described in this thesis, the optimized processing techniques for transmission and reflection holographic optical elements recorded in new AgHal materials are introduced. Diffraction efficiencies over 95% can be obtained for both transmission and reflection diffraction gratings. The main advantage of the SHSG process is that high sensitivity recording can be performed employing laser wavelengths anywhere within the visible spectrum. Other important features of SHSG emulsion developed in this work are high efficiency, low scattering and printout stability. This simplifies the manufacturing of high-quality, large-format HOEs, including also high-quality display holograms of the transmission and reflection type, and both monochrome and full colour.

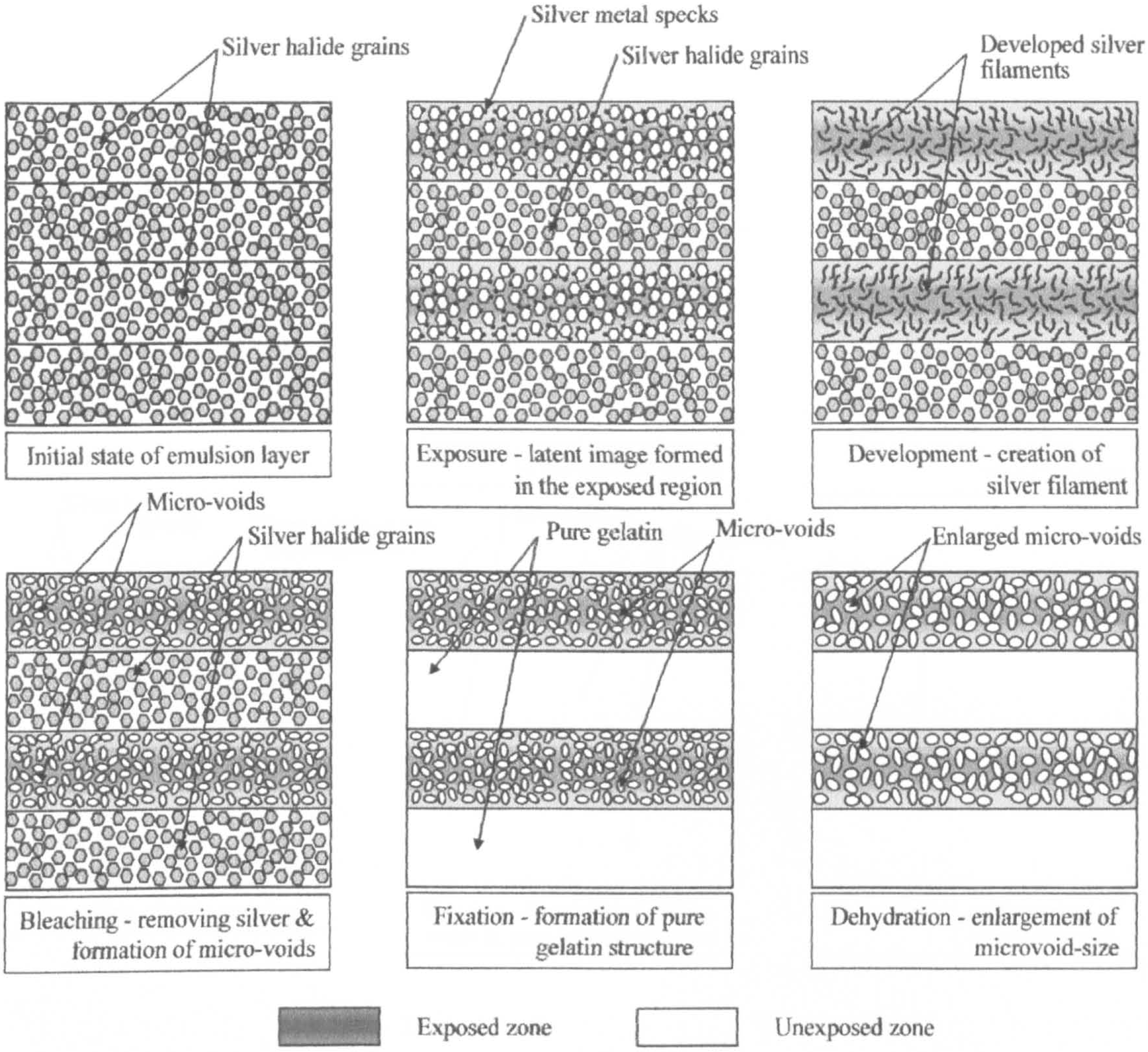

Fig. 1. 1 Schematic diagram that explains the typical reversal (solvent) bleach – SHSG process

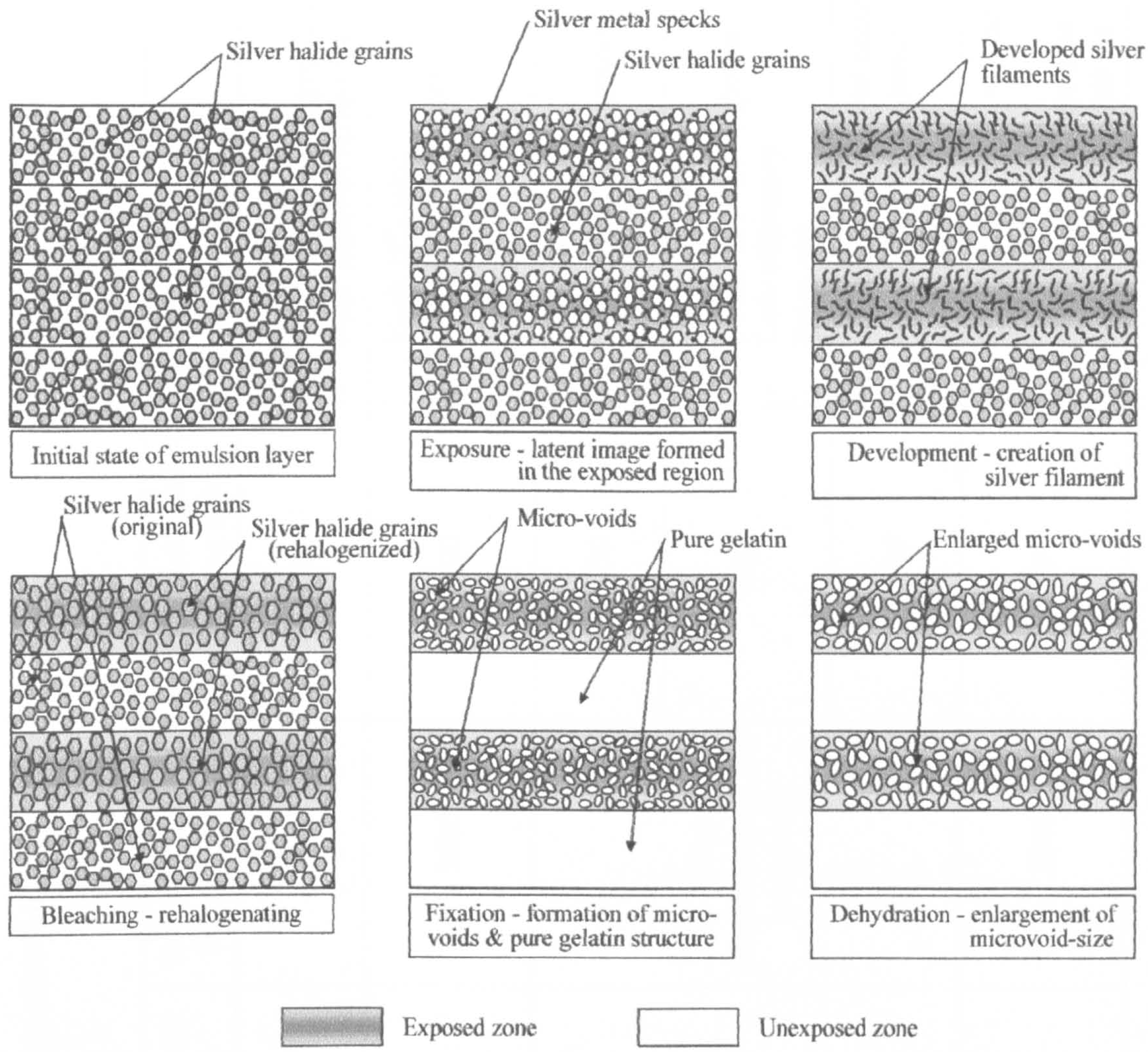

Fig. 1. 2 Schematic diagram which explains the typical rehalogenating - bleach SHSG process

Table 1. 1 Characteristics of typical holographic recording materials.

<table>
<tr><th>Materials</th><th>Typical spectral sensitivity λ(nm)</th><th>Peak sensitivity (mJ/cm^2)</th><th>Resolving power (line pairs/mm)</th><th>Maximum efficiency of grating η(%)</th><th>Remarks</th></tr>
<tr><td>Photopolymer</td><td>UV ~ 700</td><td>10^0 ~10^1</td><td>~ 1500</td><td>~ 95</td><td>- High efficiency
- Self-development process
- Poor material reliability</td></tr>
<tr><td>Photoresist</td><td>UV ~ 500</td><td>10^1 ~10^3</td><td>< 3000</td><td>~ 90</td><td>- High efficiency
- Low spectral response in visible spectrum
- Surface relief only</td></tr>
<tr><td>Silver halide emulsion</td><td rowspan="3">400 ~ 700</td><td rowspan="3">10^{-1} ~10^0</td><td rowspan="3">~ 10000 (depending on the grain size)</td><td>~ 30</td><td>- High sensitivity
- Broad spectral response
- Low efficiency</td></tr>
<tr><td>Bleached silver halide emulsion</td><td>~ 60</td><td>- High sensitivity
- Broad spectral response
- Low efficiency
- Print-out</td></tr>
<tr><td>Silver halide sensitized gelatin</td><td>~ 95</td><td>- High sensitivity, low noise
- Broad spectral response
- High efficiency</td></tr>
<tr><td>Dichromated gelatin</td><td>320 ~ 520</td><td>10^1 ~10^2</td><td>~ 3000</td><td>~ 95</td><td>- High efficiency, low noise
- Low sensitivity
- Limited spectral response
- Weak in humid condition</td></tr>
</table>

1.2 History of SHSG Processing

An overview of existing processing techniques has been publicized in the book by Bjelkhagen. [1.16] The rest of this section gives a review of SHSG processing, which summarizes the work summarized by him and cites some papers which have been published after his work.

The first attempt to form a SHSG processed phase volume hologram had been started in the 1970s by Pennington *et al.* [1.17]. They proposed a complicated, 21-step chemical process including dichromating and re-exposing. However, from the early 1980s, the process became more controllable. Graver *et al.* used Kodak 649-F plates to present a simpler method based on Kodak D-19 developer and the R-9 bleach [1.18] Chang and Winick [1.19] published a slightly different processing method to create SHSG holograms on 649-F plates. The difference between the two methods lies in the bleach solution. Chang and Winick used rehalogenating dichromated bleach bath (modified version of the Kodak R-10 bleach) instead of reversal bleach that Graver *et al.* used in their work

The SHSG processing for Agfa holographic materials was reported by Fimia *et al.* [1.20] In general the thinner and harder Agfa emulsion was found to be more difficult to use than the Kodak 649-F plates. For the process, Kodak D-8 developer (modified Kodak R-10 bleach) and the nonhardening F-24 fixer have been used. As the process temperature became higher, the diffraction efficiency was increased compared to that obtained for room temperature solutions. However, the signal-to-noise ratio decreased as the temperature increased. They used a washing bath of a slightly higher than room temperature (30°C) as well as a dehydration bath at an elevated temperature (60°C). Some interesting results have been revealed in three other publications from the Spanish research group, Boj *et al.* [1.21] and Fimia *et al.* [1.22, 23]. The influence of the bleach bath temperature was investigated. The DE obtained for a transmission grating was higher for HOEs processed at 50°C (η = 80%) than at 20°C (η = 40%). As regards reflection holograms, the so-called PAAP developer [1.24] was recommended. With the PAAP developer better resolution can be obtained. The performance at high spatial frequencies is improved which is important for reflection SHSG holograms.

Angell [1.25] introduced a 13-step processing scheme intended for the Kodak 649-F material. Later the process was slightly modified. [1.26] The complicated and time-consuming procedure contained some very interesting aspects of SHSG-processing. So far, the main tanning bleaches used were the dichromate bleaches (Kodak R-9 or R-10). Angell claimed that potassium chlorochromate (Peligouts salt) used as a bleaching agent was an improvement. This is part A of the Kodak chromium intensifier (Kodak CIA). In addition, he claimed that a fixer with a hardener could improve the dynamic range and the signal-to-noise ratio. Angell's processing scheme contained some new details, such as stabilization and emulsion protection, for example. In particular, the use of an organo-silane coupling agent (Dow Corning Z-6020) in the fixing step makes it possible to maintain the emulsion thickness after the processing, which is important for many HOE-applications. The organo-silane coupling agent N-(2-aminoethyl)-3-amino-propyltrimetohoxy silane was recommended since it is compatible with the gelatin matrix. The emulsion thickness controlling technique makes it possible to obtain a permanent chemical way of controlling emulsion thickness in holographic emulsions. However, the actual method depends on the emulsion type, the silver halide solids loading, the exposure level, the bleaching technique, etc. For example, for the Kodak 649-F emulsion, Angell found that adding 2% to 4% of the coupling agent to the fixer resulted in an emulsion thickness of 16 μm after drying, which was equal to the original thickness. Another option is to use the Kodak C41 stabilizer, which consists of two parts. Part A is a formaldehyde hardener and part B an organosilicon agent. The stabilizer can be utilized in the SHSG process to control emulsion thickness.

Weiss and Millul [1.27] and Weiss *et al.* [1.28] published a simpler SHSG processing method for the 649-F emulsion. The authors introduced the CW-C2 developer [1.28] to the SHSG process. They tested both reversal and rehalogenating dichromate bleach solutions. Weiss and Millul compared the D-19 developer with the CW-C2 developer and found that CW-C2 gave significantly higher signal-to-noise ratios. The CW-C2 developer is therefore often a better choice, in particular for reflection HOEs. As regards the bleaching part of the process, the author tested a variety of bleaching agents and found that only the reversal or the rehalogenating ammonium dichromate bleach could produce high diffraction efficiency SHSG processed HOEs.

Phillips *et al* [1.29] were able to obtain high-quality holograms using a new SHSG processing technique. The traditional view stating that the DCG system hardens gelatin, thus preventing solubilization of the material, must be balanced against other observations, such as that of the reduction of the bulk index of the gelatin layer and the appearance of gelatin in the processing solutions. The authors propose that the large values of index modulation in DCG holograms are caused by gelatin hydrolysis in the nodal parts of the image structure. Based on the new ideas about the mechanism behind the DCG process, two new processing procedures for SHSG holograms were formulated.

Very important work by Usanov *et al.* [1.30, 31] is based on the formation of a micro-cavity (MC) structure and is described in the following way. The gelatin in a photographic emulsion is adsorbed on the AgHal grains. In fact only a part of the gelatin molecules is adsorbed. The molecule chains are also linked within the gelatin mass of the emulsion. The thickness of the adsorbed layer in a dry emulsion is 2.5 to 4 nm. Each AgHal grain is surrounded by gelatin molecules linked at different points by active groups able to form complex compounds with silver grains produced during the development. The Russian method is based on the fact that these adsorbed layers are less active and will be more difficult to harden than the surrounding gelatin mass. Variations in hardening between exposed and unexposed areas will therefore occur. After removing silver and AgHal grains from the emulsion and dehydrating the hologram, micro-cavities will remain which will be responsible for the refractive index variations. The processing is performed in the following way. After the material has been exposed, developed and fixed, it is hardened in a potassium dichromate solution or in formaldehyde. The treatment in the hardening solution takes one-hour or more in the potassium dichromate bath. The duration of treatment is six times longer in the formaldehyde solution. After that the material is bleached, fixed and finally dehydrated. Another possibility is to bleach the material before hardening it. After that it is fixed and dehydrated. A third possibility is to use reversal bleach after development. Then the material is hardened and the final steps are fixing and dehydration. The second processing method results in holograms with better spectral selectivity than holograms processed according to the third method. The new SHSG technique was tested using the Russian material PFG-03. High quality holograms were produced with diffraction efficiencies between 70% and 90% at 458 to 647 nm. It is mentioned that the D-19 developer, which contains a large amount of potassium bromide (20 g/l), is a better alternative for processing reflection HOEs in the PFG-03 emulsion than the GP-2 developer, previously used [1.32].

Simova and Kavehrad [1.33, 34] introduced a modified processing technique for HOE recordings on the Agfa 8E75 HD emulsion. The processing technique was based on a 10-minute hot (75°C) wash to soften the hard Agfa emulsion. This was done after the emulsion was developed and fixed in a nonhardening fix solution. Bleaching was performed in reversal ammonium dichromate bleach at 50°C. A diffraction efficiency of about 80% could be obtained over a rather wide spatial frequency range. The authors main application was the fabrication of a 4 x 4 holographic star coupler. Extensive work on SHSG processing has been performed in Spain. Pascual *et al.* [1.35] and Fimia *et al.* [1.36] have described the advantages of using rehalogenation of the silver image as an important feature of the SHSG process. Since silver is not removed from the developed site when rehalogenation of the silver takes place, the formation of hardened shells around the bleached silver site is enhanced by non-removal of the contents of each shell, as explained by Phillips *et al.* [1.29] An optimized process for the Agfa 8E75 and 8E56 HD materials was published by Fimia *et al.* [1.37] in which a modified R-10 bleach (at 50°C) was used. It was shown that the PAAP developer produces HOEs with lower noise and better diffraction efficiencies at higher spatial frequencies as compared to the D-19 developer.

In another publication by Fimia *et al.* [1.38] the authors investigated how to optimize the SHSG process by studying the HOE diffraction efficiency in a water tank before dehydration. In addition, they introduced the AAC developer (ascorbic acid - sodium carbonate), which avoids the influence of oxidation products during development. By measuring the diffraction efficiency at different stages during the process it was possible to find, e.g., the optimal potassium bromide concentration in the R-10 bleach. A diffraction efficiency of 80% for diffraction gratings (1000 lines/mm) recorded on Agfa 8E56 HD emulsion at 514nm wavelength was obtained. The material was processed in the ACC developer, bleached in the optimal R-10 bleach, fixed in Kodak F-24 fix, and dehydrated in isopropanol in the usual way. It is known that the cross-linking of gelatin is not very effective in highly acid bleach baths (such as the R-10). By interrupting the process after the bleaching step (without washing the plate) and leaving the plate in high humidity for 24 hours Fimia *et al.* [1.39] reported a better spatial frequency response for SHSG processed Agfa materials. The SHSG process for diffuse-object recording has been investigated by Fimia *et al.* [1.40-43]. The inclusion of noise gratings as a new source of noise in SHSG processing was discussed. In particular, they concluded that to understand its influence on the signal-to-noise ratio may require new models.

The most recent progress in SHSG processing has been reported by Beléndez *et al.* [1.44-46] and Neipp *et al.* [1.47] regarding the new German HRT red-sensitive BB-640 emulsion of the ultrafine-grain AgHal type (grain size about 25 nm). The high diffraction efficiency (over 90%), extended spectral frequency response (e.g., DE 40% for Agfa as compared to DE 85% for BB-640 at 2800 lines/mm) and high S/N ratios indicate the importance of SHSG processing for HOE manufacturing in the future. In another publication, Neipp *et al.* [1.48] have investigated the influence of the development in SHSG processed Slavich PFG-01 plates.

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Chapter 2

Transmission HOEs Recorded in SHSG Emulsions

2.1 Introduction

As has been discussed in Chapter 1, HOEs are often recorded in dichromated gelatin, which offers high DE (diffraction efficiency) combined with low noise. The drawback of DCG is its low sensitivity and limited spectral response. Therefore, considerable attention has been directed at using AgHal materials processed in such a way that the final hologram will have properties like a DCG hologram. This can be achieved using special processing techniques (SHSG), which produce low-scatter HOEs of high efficiency. In addition, the SHSG hologram is printout-free. Recently, this technique has become more important because of the appearance of ultra-high resolution silver halide emulsions manufactured by e.g., Slavich [2.1] in Russia and Holographic Recording Technologies [2.2] in Germany. Employing such materials, HOEs can be manufactured with a quality more or less equal to HOEs recorded on DCG materials.

In this chapter, primarily SHSG techniques that work well for transmission HOEs will be described. Summarizing the SHSG process, AgHal emulsion is exposed, developed and bleached sequentially. In most cases tanning dichromate bleach is used. A pure gelatin structure is formed by the fixing step removing all the AgHal grains from the emulsion. The last step of the processing is to dehydrate the emulsion using isopropyl alcohol in the same way in which dichromated gelatin holograms are processed.

2.2 AgHal Materials for Transmission SHSG

Agfa is no longer producing holographic materials, however, the company manufactures a lithographic emulsion (Millimask) which is similar to the former holographic Holotest 8E56 HD material. The recording materials used in these experiments are commercial

AgHal materials currently obtainable on the market: Agfa Millimask, Slavich VR-P and Slavich PFG-03C. The Millimask and VR-P are similar materials of the orthochromatic type while the PFG-03C is of the ultrahigh resolution panchromatic type. The main differences between the Slavich and the former Agfa holographic materials are the grain size and the silver content in the emulsion. The panchromatic Slavich emulsions have grain sizes as small as 10 nm. The former highest quality Agfa materials (Holotest HD materials) had grain sizes of about 44 nm. Millimask and VR-P have very similar grain size to Holotest HD materials. The Slavich silver content is one-half (about 0.25 g/cm^3) of the silver content in Agfa materials. Grain size is important for two reasons. It determines the resolving power of the emulsion and also strongly influences scattering.

The influence of particle size and wavelength on the scattering was investigated by Lord Rayleigh and Gustav Mie. In 1871, the first quantitative study on the scattering by small particles was done by Lord Rayleigh [2.3] and such scattering is frequently called "Rayleigh scattering". He made mathematical investigation which gave a general law for the intensity of scattered light. That theory is applicable to any kind of particles with refractive index different from that of the surrounding medium. The only limitation is that the linear dimensions of the particles should be considerably smaller than the wavelength. In 1906, Gustav Mie calculated the angular resolved scattering intensity of light scattered at spherical particles [2.4]. Actually, Mie scattering is more general than Rayleigh scattering: it occurs when (electromagnetic) radiation hits a spherical particle or a molecule whose diameter is similar or greater than the wavelength of the radiation. The theory is suitable for particles of a diameter from at least twice the wavelength of the light source. Mie scattering is not strongly wavelength dependent and produces the almost white glare around the sun when a lot of particulate material is present in the air. It also gives us the white light from mist and fog. The scattering from molecules and very tiny particles (< 1 /10 wavelength) is predominantly Rayleigh scattering. For particle sizes larger than a wavelength, Mie scattering predominates. In the case of the scattering in the ultrafine grain AgHal emulsion, Rayleigh scattering is dominant because the typical grain size is a lot smaller than the recording wavelength (about 1/40~1/70).

According to the Rayleigh's law, the scattered intensity is proportional to the incident intensity and to the square of the volume of the scattering particle. And the scattering also depends on the incident wavelength. The scattered intensity is proportional to $1/\lambda^4$. Because the red light (λ=647) has a wavelength approximately 1.4 times longer than blue light (λ=458), the scattering of blue light from particles much smaller than a wavelength should be almost 4 times greater than that of red light.

In order to obtain high-quality HOEs, Rayleigh scattering that occurs during the recording, has to be as low as possible. In particular if blue laser wavelengths are used for the recording, an ultrafine-grain AgHal material is needed. Phillips *et al.* [2.5] discuss scattering in AgHal emulsions from the concept of scattering mean free path. Photographic layers used for commercial holographic materials are normally about 7 μm thick. The emulsion consists of small AgHal crystals in a gelatin matrix. According to the law of Rayleigh scattering, the light scattering from these crystals would be proportional to Δ^6/λ^4, where Δ is the diameter of the grain and λ, the wavelength. If the radius of the AgHal crystals (assumed spherical) is a and the number per unit volume of the layer is N, then

$$\frac{4\,d\,N\pi\,a^3\,\rho}{3} = m_{AgH} \tag{2-2}$$

where ρ denotes the density of silver halide, m_{AgH} is the mass of silver-halide per unit area, and d is the thickness of the emulsion. The atomic weight of silver is 108 and that of bromine is 80. So the mole fraction of Ag in AgBr is 108/188. So

$m_{AgH} = (188/108) m_{Ag}$,

$m_{Ag} = 5$ g/m^2 (for Agfa materials),

$\rho_{AgBr} = 6.47$ g/cm^3.

A increase in grain size usually means that the same amount of silver bromide would be shared between fewer but larger grains which, in turn, means that Na^3 is constant. For the former Agfa materials

8E-materials: grain diameter $2a = 44$ nm $\rightarrow$ $N_{8E} \sim 4 \times 10^{15}$ grains/cm^3,

10E-materials: grain diameter $2a = 90$ nm $\rightarrow$ $N_{10E} \sim 5 \times 10^{14}$ grains/cm^3.

For the Slavich material,

PFG-03C: grain diameter $2a = 16$ nm $\rightarrow$ $N_{PFG\text{-}03C} \sim 2 \times 10^{17}$ grains/cm^3.

The scattered intensity I_s of light off these small particles is S $\propto$ Nda^6. But since Na^3 is constant for a certain material, I_s is therefore $\propto a^3$, which means that light-scattering varies with the cube of the grain size. Phillips *et al.* [2.5] have introduced a parameter ξ denoting the ratio of scatter mean free path to the emulsion thickness which can be used as a figure of merit to describe the holographic recording layer, namely

$$\xi = 1/(N\,\sigma_{RS}\,d), \tag{2-3}$$

where N denotes the number of grains per unit volume, d the emulsion thickness, and σ_{RS} the Rayleigh scatter cross section being

$$\sigma_{RS} = \frac{\pi}{12}\cdot\left[\frac{2\pi\cdot n_G}{\lambda_a}\right]^4\cdot\left[\frac{(n_H/n_G)^2-1}{(n_H/n_G)^2+2}\right]^2\cdot(2a)^6 \tag{2-4}$$

with λ_a being the wavelength of the light in air, n_G the refractive index of gelatin (n_G = 1.54), n_H the refractive index of halide grain ($n_{AgBr} = 2.236$), and 2a, the grain diameter. The emulsion thickness for the Agfa materials as well as the Slavich materials is about 7 µm. The calculations are performed using the sodium line wavelength (λ = 589 nm). The numerical values of ξ are:

Agfa 8E-materials ≈ 3

Agfa 10E-materials ≈ 0.3

Slavich PFG-03c ≈ 55

The 8E-material is just on the border of acceptability for recording holograms, but the 10E is not really acceptable for high-spatial frequency recordings. The ξ parameter of Slavich emulsion indicates that this material is considerably better than the Agfa emulsions.

Neipp *et al.* [2.6] found the ξ parameter for BB-640 (grain diameter 22 nm) [2.2] to be about 85 ($\lambda = 633$ nm). The Slavich material is similar and considerably improvements are obtained by using such ultra-high-resolution materials. The Agfa Millimask material is similar to the 8E emulsion but has dyes in the emulsion to reduce scattering, which may help in recording transmission HOEs. Transmission HOEs can be recorded in both Millimask and the similar Slavich VR-P emulsion. Reflection HOEs are more critical and require the lowest light scattering AgHal materials for highest possible DE. In regard to reflection HOEs more details will be covered in the next chapter.

2.3 Materials Used in Transmission SHSG Processing

This section reviews the specific materials used in this work. The orthochromatic Agfa-Gevaert Millimask HD FL5 emulsion has its colour sensitivity peaked at 525 nm. It is a high contrast material with a gamma of about 5.00. The grain size is about 45 nm for the HD material. The HD (High Definition) emulsion has an improved line edge gradient, which means a sharper edge to the lithographic lines. This feature is important for micro-lithography work that is the main application for the Millimask materials. Antihalation action is provided by a volumetric dye that forms part of the emulsion.

The orthochromatic Slavich VR-P emulsion is similar to the Millimask material. Mainly, it is intended for recording holograms of the transmission type. The emulsion's spectral sensitivity $S(\lambda)$ is useful from 488 nm to 532 nm. The grain size is between 35 nm and 40 nm. An antihalation coating on the back of the material provides antihalation action. The sensitivity S of VRP measured at 514 nm is $S \approx 75\ \mu J/cm^2$.

The panchromatic Slavich PFG-03C emulsion is intended for the recording of colour holograms. The emulsion's useful spectral sensitivity is from 450 nm to 700 nm. The grain size is between 10 nm and 20 nm. There is no antihalation coating since the material is intended for the recording of both transmission and reflection holograms. The sensitivity S $\approx$ 2 to 3 mJ/cm^2 measured at 514 nm.

The D-log E curves for these emulsions are shown in Figure 2.1, which were obtained by recording amplitude diffraction gratings with two beams interfering with each other at an angle of 30° using s-polarized light from an Ar-ion laser (λ = 514.5 nm). To avoid internal substrate reflections an index matching fluid (Dekalin solvent, n = 1.475) was applied between the emulsion substrate and a light-absorbent black glass plate underneath it.

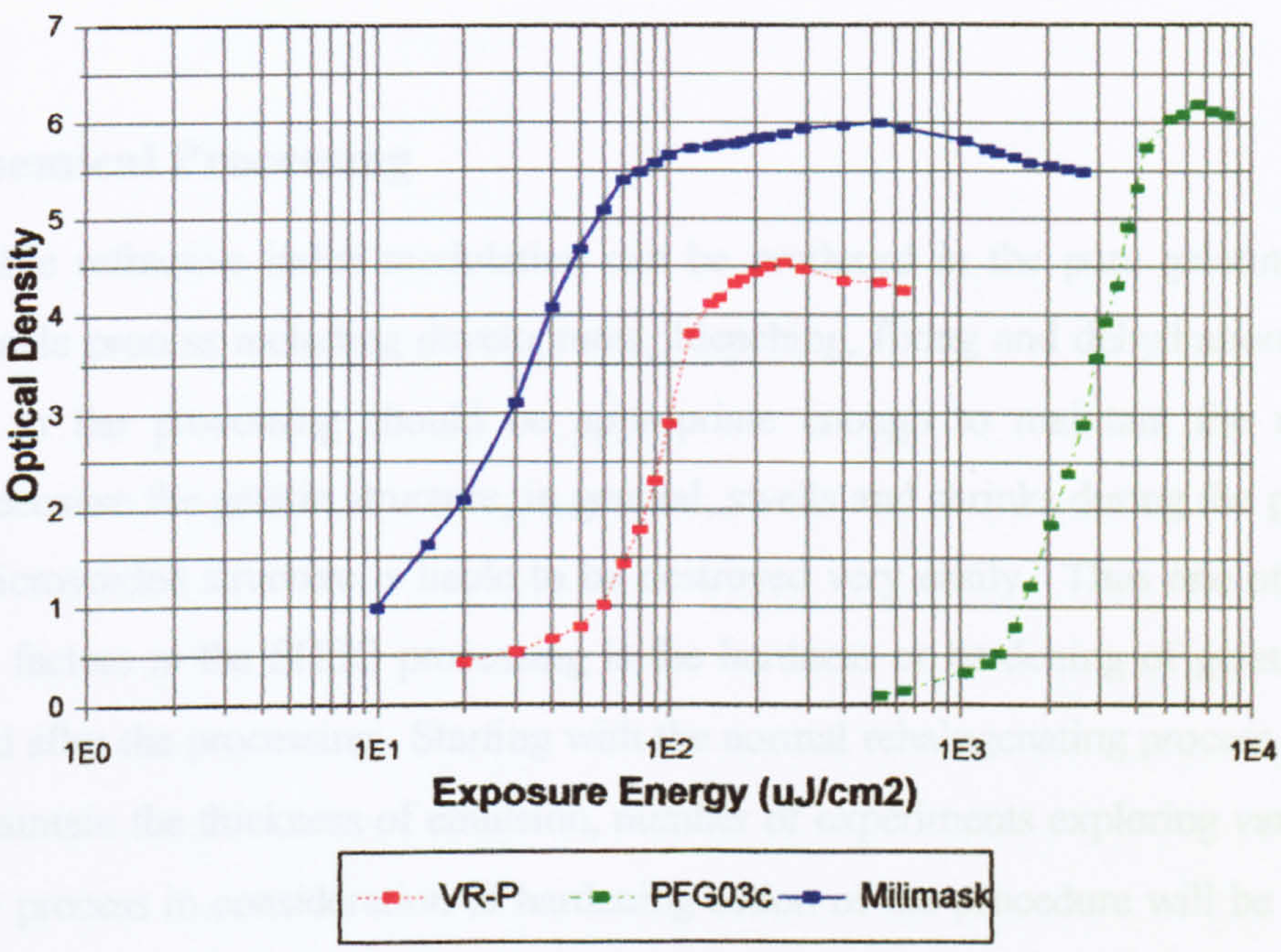

Fig. 2. 1 Optical density of plates used in SHSG processing.

The procedure of making amplitude hologram is as follows:

- Exposure (incident intensity 100μW/cm^2, with various exposure times)
- Develop (1:4 diluted Agfa G282c, lithographic developer, for 3 min @ 20°C)
- Wash (3 min in running distilled water)
- Fix (1:4 diluted Ilford HYPAM Fixer with Rapid Hardener, diluted 1: 40, for 2 min @ 20°C)
- Wash (5 min in running distilled water)
- Dry (1 hour in high humid desiccator with in excess of 60% RH)
- NB. Ilford Rapid Hardener contains aluminum chloride.

2.4 Transmission SHSG Processing and Emulsion Hardening

2.4.1 Chemical Processing

Considerable refractive index modulation can be produced in the pure gelatin structure using suitable process including development, bleaching, fixing and dehydration step. All the steps in the processing should be appropriate enough to maintain the microvoid structure because the gelatin structure, in general, swells and shrinks during the processing i.e. the microvoided structure is liable to be destroyed very easily. Thus one of the most important factors in the SHSG processing is the hardness or hardening of gelatin before, during and after the processing. Starting with the normal rehalogenating process since it is easy to maintain the thickness of emulsion, number of experiments exploring variations of the SHSG process in consideration of hardening action of the procedure will be described later. The normal rehalogenating process is illustrated in Table 2.1.

Table 2. 1 Normal rehalogenating process for SHSG method

Steps	Solutions
Developing	Non-tanning developer
Bleaching	Rehalogenating (tanning dichromate) bleach
Fixing	Non-hardening fixer
Dehydration	Series of solvent bath

2.4.2 Effect of Gelatin Hardening Before and During Processing

In DCG holograms, the refractive index modulation occurs in two phases: the re-arrangement of gelatin chains and the formation of voids in the unhardened areas. Unlike the situation as regards DCG processing, the SHSG process is based on the fact that microvoids formed during processing remain in the gelatin after processing, which constitute the refractive index modulations. The microvoid structure that remains after processing can easily collapse during or after the processing, during the dehydration steps. The essential SHSG processing problem is how to substitute the molecules of water and isopropanol with air without emulsion shrinkage or collapse of the microvoid structure in the processed emulsion. In order to achieve this, the dry emulsion must be of appropriate hardness, which means, it can withstand the wet processing without the collapse of the microvoid structure. Hence, the key to the success in SHSG processing is how to obtain and maintain a uniform and firm structure of microvoids in the pure gelatin layer after processing and drying. It is well known that the hardening, swelling and drying technique are the most important parts of the processing steps in both transmission and reflection HOEs obtained by SHSG processing. [2.7] The main parts of the present investigation are: (1) to find the optimal hardening process, (2) to find the dehydration technique which gives uniform and high-efficiency results, (3) to optimize the SHSG process for the new AgHal emulsions.

2.4.3 Emulsion Characteristics as a Function of Hardening

The significance of the gelatin hardening process is that it reduces the tendency of gelatin to swell in water and aqueous solutions and increases the range of temperature allowed for further processing. In general, the hardness of holographic emulsion greatly affects HOE characteristics in SHSG processing. Initial hardness is the first factor to consider. The new AgHal emulsions are softer than, e.g., the earlier Agfa emulsions as well as the Millimask plates. The emulsion swells during the wet processing, and the degree of swelling depends on the initial hardness of the dry emulsion. Swelling of gelatin depends on a number of factors, e.g., internal and external osmotic effects, viscoelastic effects, etc. In addition, swelling will depend most importantly upon pH, which can influence these effects. Minimum swelling occurs at or near the solution's isoelectric point.

In the performance of SHSG processing of the former holographic Agfa 8E75 HD emulsion, it was recommended to presoak the plates in a warm water solution before exposure in order to obtain desired results. [2.8] As regards the new AgHal emulsion BB-640; hyper sensitization was needed before exposure in order to obtain the best results. [2.9] If the Slavich plates having a rather soft emulsion are processed without prehardening, the emulsion can be damaged during washing or drying process. Thus the control of hardness throughout the SHSG process, i.e. swelling and shrinkage, is essential in order to achieve good results.

2.4.4 Influence of pH on Hardening and Efficiency

A number of factors that influence the rate and degree of hardening or tanning of proteins are pH dependent. If chromium is introduced in the gelatin in a bleach bath of high acidity, the tanning effect is low. In aqueous solution basic chromate salts aggregate gelatin to a high degree in the 4.5 to 5 pH range. For the chrome hardening agents usually employed there is a certain upper limit to the pH values of the solutions. This is caused by the fact that the incorporation of too many hydroxyl groups in the chromium complex will lead to a high degree of aggregation which then makes the tanning compound too bulky for effective emulsion permeation and hence hardening. What is normally taking place in an acid bleach bath is that dichromate is absorbed into the bleach bath and reduced to trivalent chromium by the developed image silver. It has been suggested that the tanning can only occur in a subsequent washing bath that has a pH value of about 5. [2.10] In this case the pH of the bleach solution is so low that the swelling of emulsion is considerable and the rinse in distilled water exacerbates the problem of swelling as well.

This investigation was focused on the hardening process before development and during the bleach procedure. Initially various hardening agents were tested, such as, e.g., chrome alum, potassium alum and formaldehyde solution. The pH value was adjusted somewhere between 4 and 6. Unfortunately, good results could not be achieved with those chemicals except formaldehyde, although they are regarded as good hardeners for photographic emulsions. The degree of hardening with chrome alum is greater than that with potassium alum. The former solution was very unstable and, thus, it is difficult to control the degree of hardening. Other auxiliary hardening solutions tested contained aluminum nitrate, chromium III chloride and ammonium chloride respectively. The formaldehyde hardening solution was found the best when producing SHSG holograms using the PFG-03C plates. The pH value was adjusted to about 5 in order to obtain maximum hardening with formaldehyde bath. The following bath is used for the first prehardening step:

Formaldehyde 37% (Formalin)	10 ml (10.2 g)
Potassium bromide	2 g
Sodium carbonate (anhydrous)	5 g
Deionized water	1 l

The results of the prehardening tests are shown in Fig. 2.2. PFG-03C plates were prehardened in formaldehyde solution varying the treatment time. The DE measurements have been done using a measuring system with goniometer, which is shown in Fig. 2.3. And the SHSG processing was according to the procedure described in Table 2. 2.

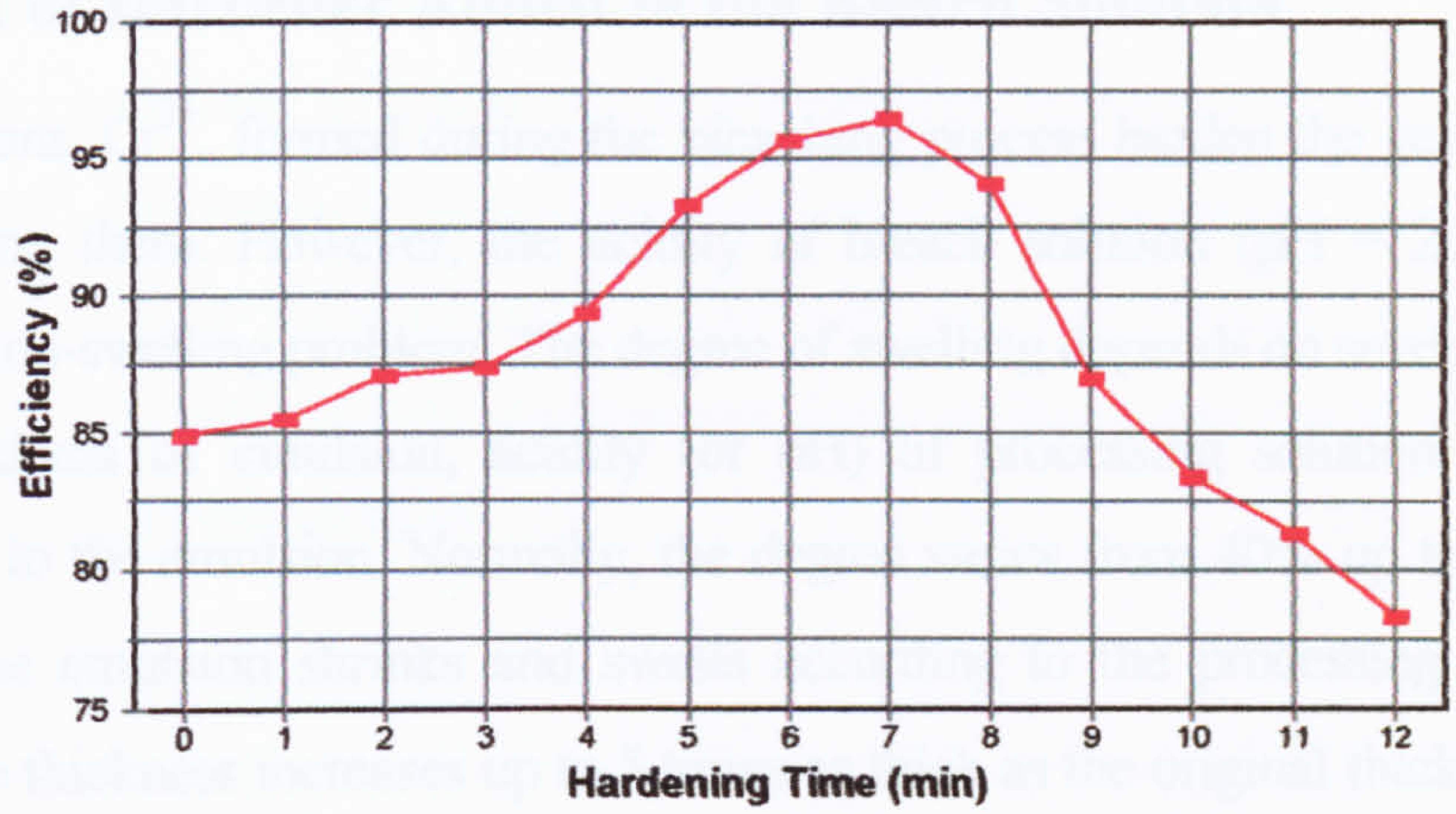

Fig. 2. 2 DE of PFG03c plate hardened in Formalin solution

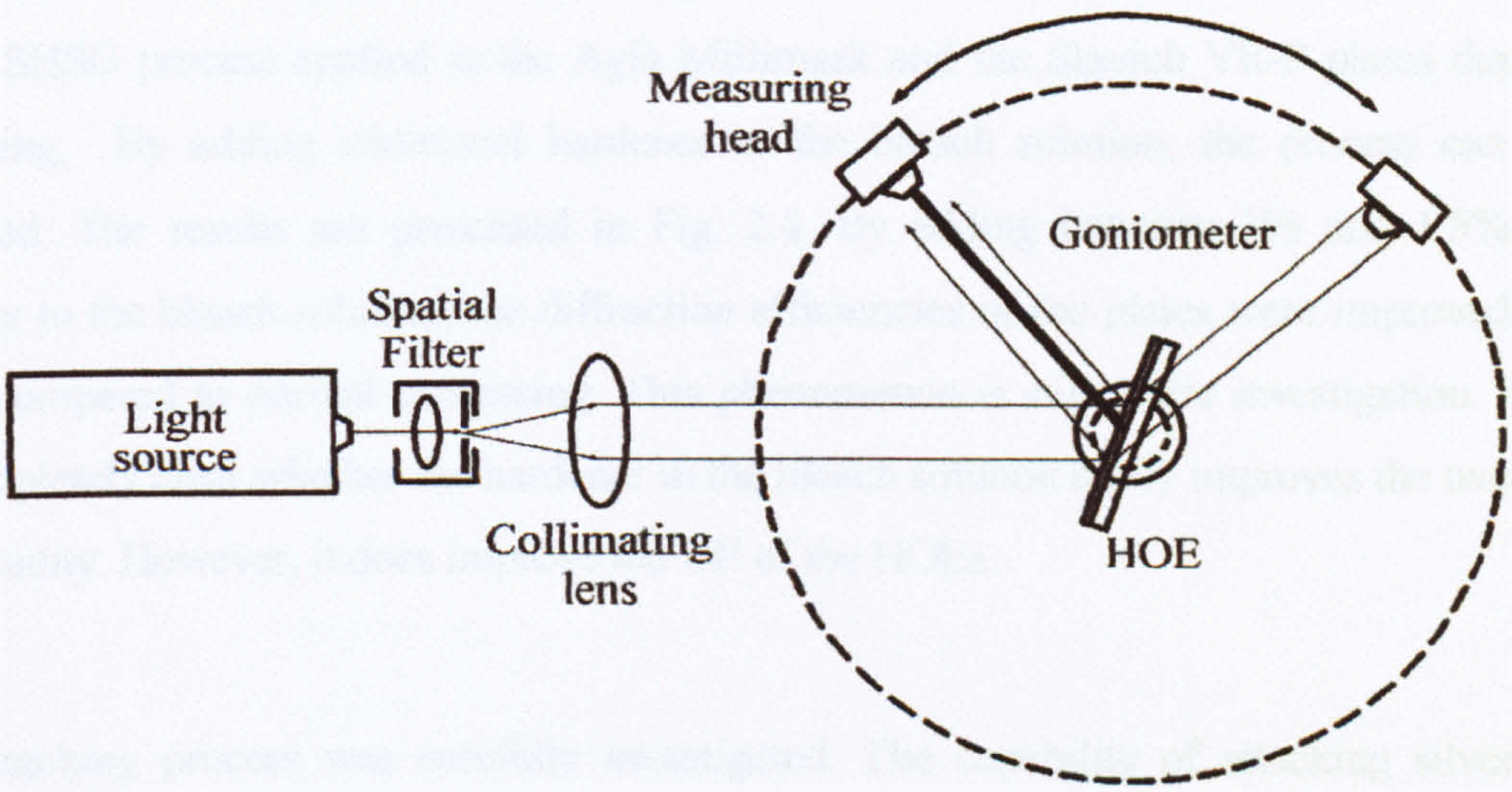

Fig. 2. 3 DE measuring system using goniometer

These results show that high DE can be obtained only when the holographic plate possesses appropriate hardness before and during the SHSG processing. If the gelatin is too soft, the microvoids formed in the gelatin structure will collapse or be destroyed. On the contrary, if it is too hard, the amplification of microvoids does not occur during the drying process. According to this fact, it is very important to fully understand the behavior of the AgHal emulsion. These aspects will be further studied when investigating SHSG processed HOEs of the reflection type.

2.4.5 Effect of Hardener Added in the Bleach Solution

The chrome ions, Cr^{3+}, formed during the bleaching process harden the gelatin molecules by cross-linking them. However, the acidity of bleach solution (pH = 2.5~3) causes a serious emulsion-swelling problem. The degree of swelling depends on several factors such as initial hardness of emulsion, acidity (or pH) of processing solution and chemical concentration in the emulsion. Normally, the degree varies from 40% up to 300%, which means that the emulsion shrinks and swells according to the processing condition and sometimes the thickness increases up to 5 times as thick as the original thickness. Thus the pH should be controlled during the processing. If the pH is adjusted to about 5, the chromium ions reduce in number and the bleaching will not proceed.

The effects of hardening have been investigated to find the optimum hardening condition for the SHSG process applied to the Agfa Millimask and the Slavich VR-P plates during processing. By adding additional hardener to the bleach solution, the process can be improved. The results are presented in Fig. 2.4. By adding between 1% and 1.5% of hardener to the bleach solution, the diffraction efficiencies of the plates were improved up to 5% compared to normal processing. This phenomenon is still under investigation. It is not completely clear whether the hardener in the bleach solution really improves the overall HOE quality. However, it does improve the DE of the HOEs.

The bleaching process was carefully investigated. The capability of attacking silver in gelatin layers and hardening of gelatin by chrome and aluminum ions has been studied. Various chemicals, such as, e.g., chromium chloride, aluminum chloride, and aluminum nitride were added in the bleach in order to enhance the hardening process. The gelatin molecule cross-linking process depends on the number of the Cr^{3+} ions and in particular the pH of the bleach solution. The acidic nature of the bleach solution tends to move the pH on the acidic side of the optimum for the hardening process (pH~5).

Extra Cr^{3+} ions have been introduced by adding, for example, chromium (III) chloride or chromium (III) nitrate to the bleach solution. Trivalent aluminum ions by the addition of, e.g., aluminum (III) chloride or aluminum (III) nitrate can also be introduced to the bleach.

Trivalent ions derived in this way are not dependent on the local density of developed silver and, thus, are not known to enhance the differential hardening effects of the tanning bleaches. These compounds are commonly used in hardening fixer solution for photography. The obtained DE results for HOEs produced in augmented tanning bleach are presented in Fig. 2.4. Addition of extra cross-linking ions has an increasing effect on the DE of HOEs processed by this process.

2.5 Drying Methods in SHSG Processing (Drying Process Using Various Solvents)

The most important variables in SHSG process, which directly influence the characteristics of the SHSG hologram, are the degree of emulsion hardness during the wet processing as well as the condition of the drying process. In particular, both the temperature and the speed of drying affect the characteristics and the uniformity of the SHSG hologram. That is, how to substitute the molecules of isopropanol and water contained in the emulsion during the wet processing with air molecules in the last dehydration step.

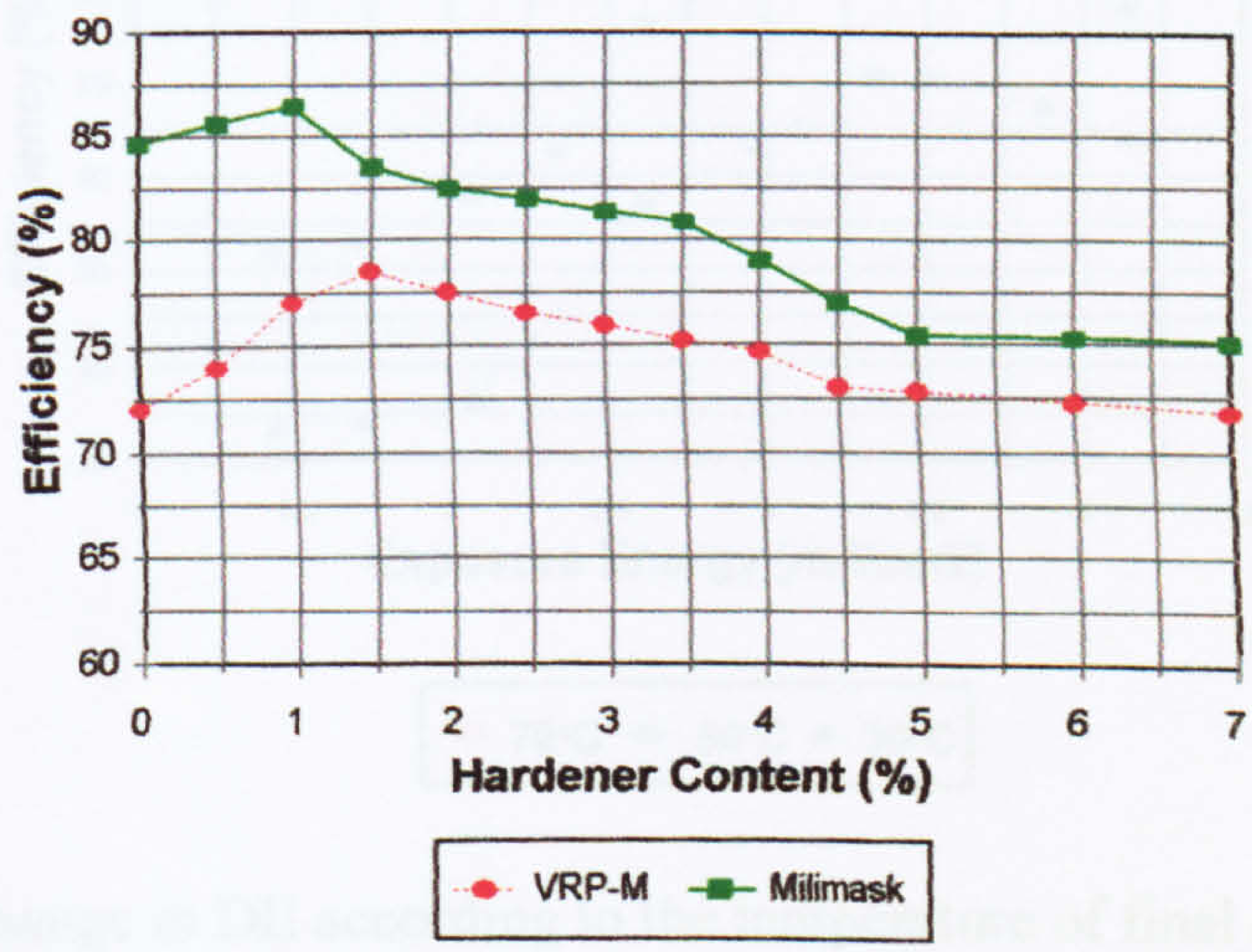

Fig. 2. 4 The effect of hardener in the bleach solution

During the final drying step, i.e., when the plate is brought out of the hot isopropanol bath, a sudden transition has been observed, which is like a sudden extraction of vapor from the gelatin layer. This only occurs when the temperature of the hot isopropanol bath is close to its boiling point. Only at that temperature the vapor pressure of isopropanol exceeds the atmospheric pressure, and then the isopropanol vapor can be extracted from the microvoid in the gelatin layer. The sudden extraction causes the amplification of microvoids. [2.11]

The effect of the drying process temperature was investigated. The obtainable DE as a function of final drying bath temperature is shown in Fig. 2.5. When the isopropanol temperature reaches the boiling point, the highest DE is obtained. These results are in agreement with the results of Usanov *at al.* [2.8] In these results, there is an interesting effect on latitude of the efficiency. As the temperature of final dehydration bath got higher, the latitude became broader. This effect seemed to be caused by the enlargement of the microvoids, which resulted in the decline of fringe-definition in the emulsion.

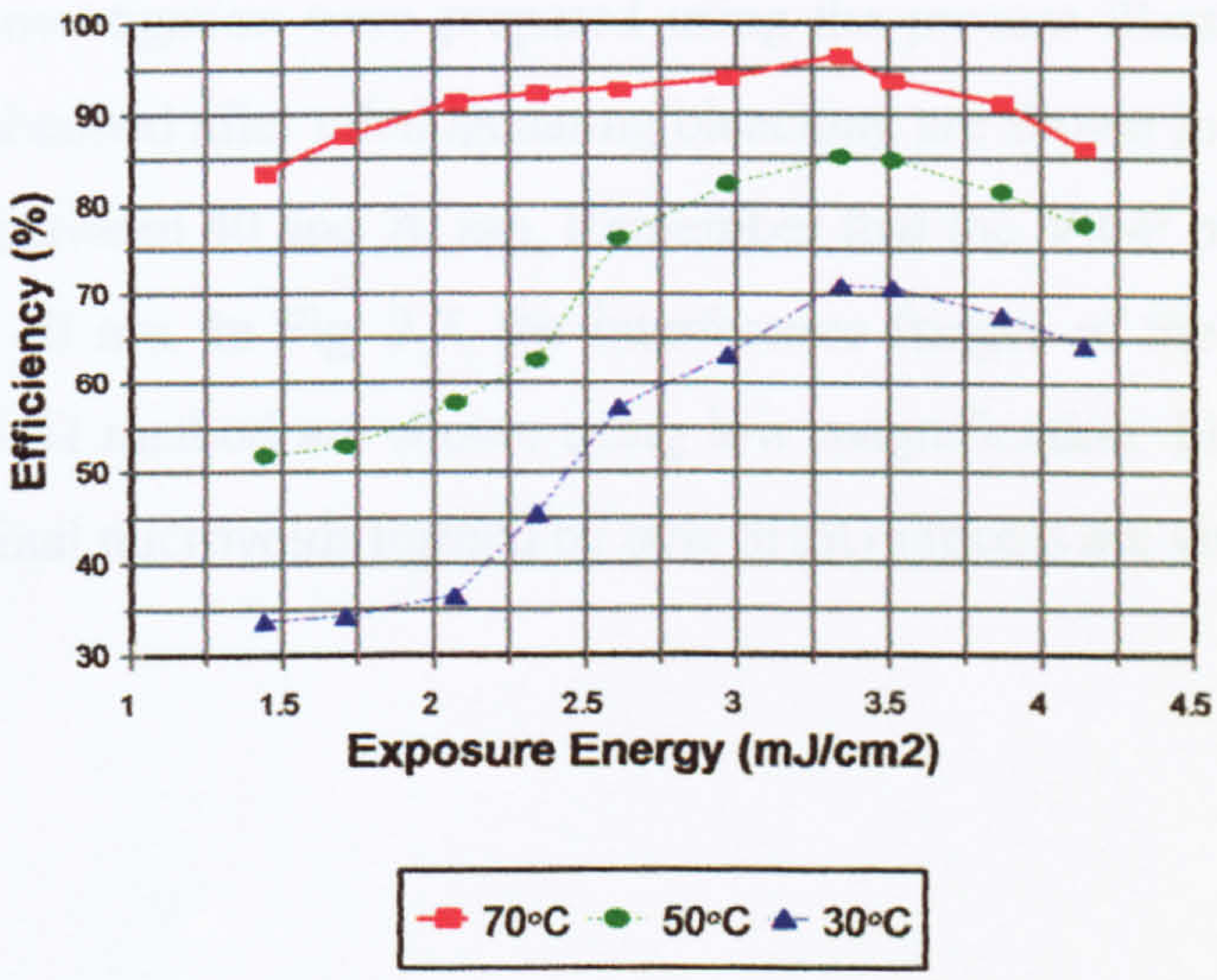

Fig. 2. 5 Change in DE according to the temperature of final drying bath.

Other solvents, such as, methanol, and ethyl-methyl-ketone (Butan-2-One) have been examined as well as different drying procedures. Although the saturation vapor pressure of methanol is higher than that of any other solvents examined, the DE of a SHSG hologram processed in methanol is lower than that of holograms processed in isopropanol. When methanol was introduced in any sequence of the drying process, ripple defects affected the surface of the gelatin. The saturation vapor pressure of ethyl-methyl-ketone is much lower than that of methanol, the results using ethyl-methyl-ketone was better than methanol, although, not as good as using isopropanol. Ethyl-methyl-ketone tends to attack film substrates, which means, this solvent is not applicable for processing holographic emulsions coated on film substrates, such as, e.g., tri-acetate film. In conclusion, isopropanol seems to be the best solvent that can be used in the final dehydration step of SHSG processing.

2.6 Transmission Electron Microscopy Investigation

In order to show the microstructure of processed SHSG emulsion, transmission electron microscopy investigations of some of the Slavich VR-P plates have been performed. The samples for TEM investigation were prepared using the process illustrated in Table 2.2. The AgHal grains obtained after rehalogenating bleaching are shown in Fig. 2.6. The sizes of these grains are between 40 and 70 nm. Remember that the VR-P plates have a coated grain size of about 40 nm. In Fig. 2.7, the interference fringes of the diffraction grating processed using SGSH method are shown using low magnification. In Fig. 2.8, at higher magnification, the final microvoids formed by new SHSG process are visible and their sizes are about 70 nm.

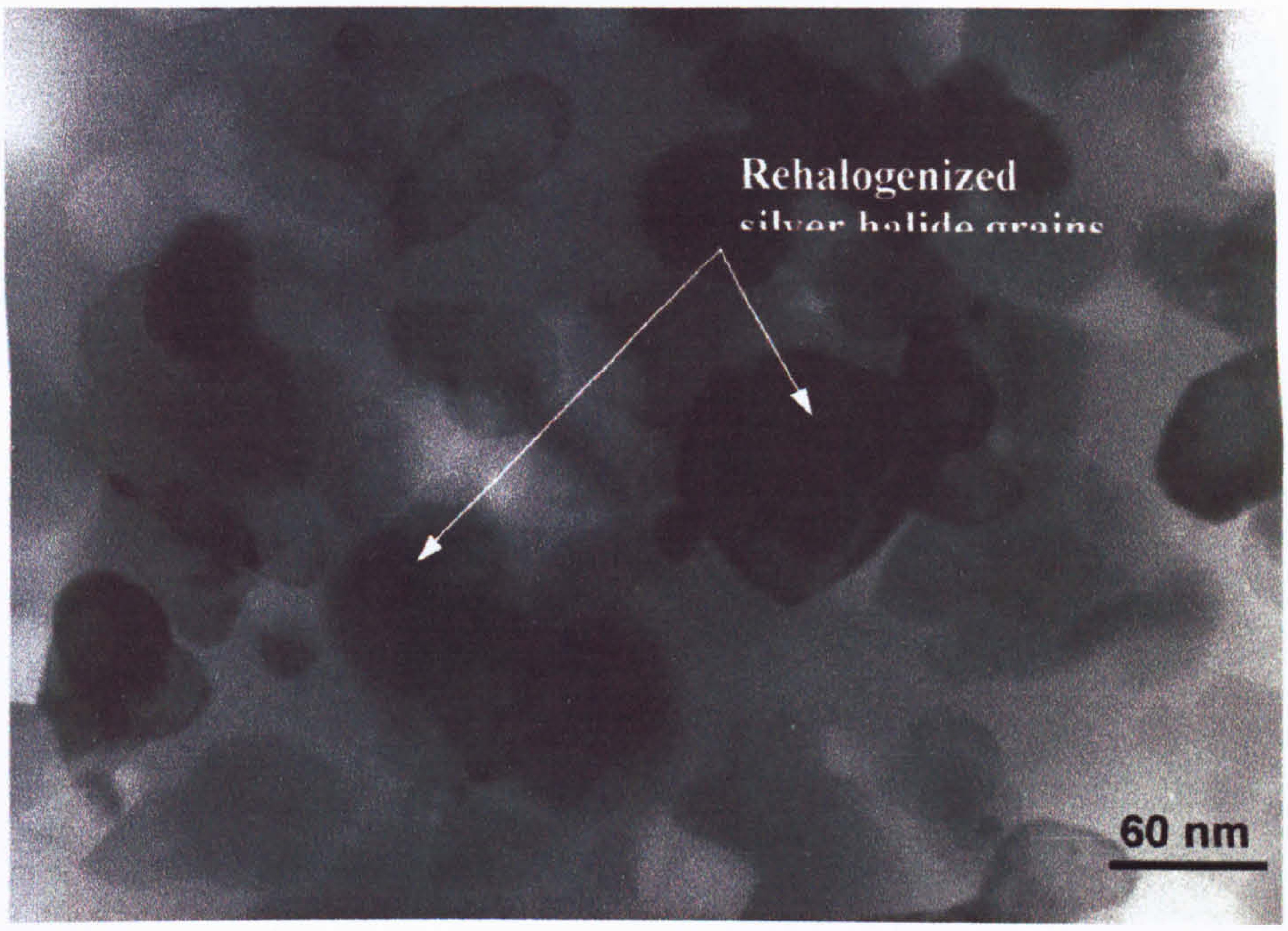

Fig. 2. 6 Cross-sectional TEM image of bleached VR-P plate processed using the rehalogenating method.

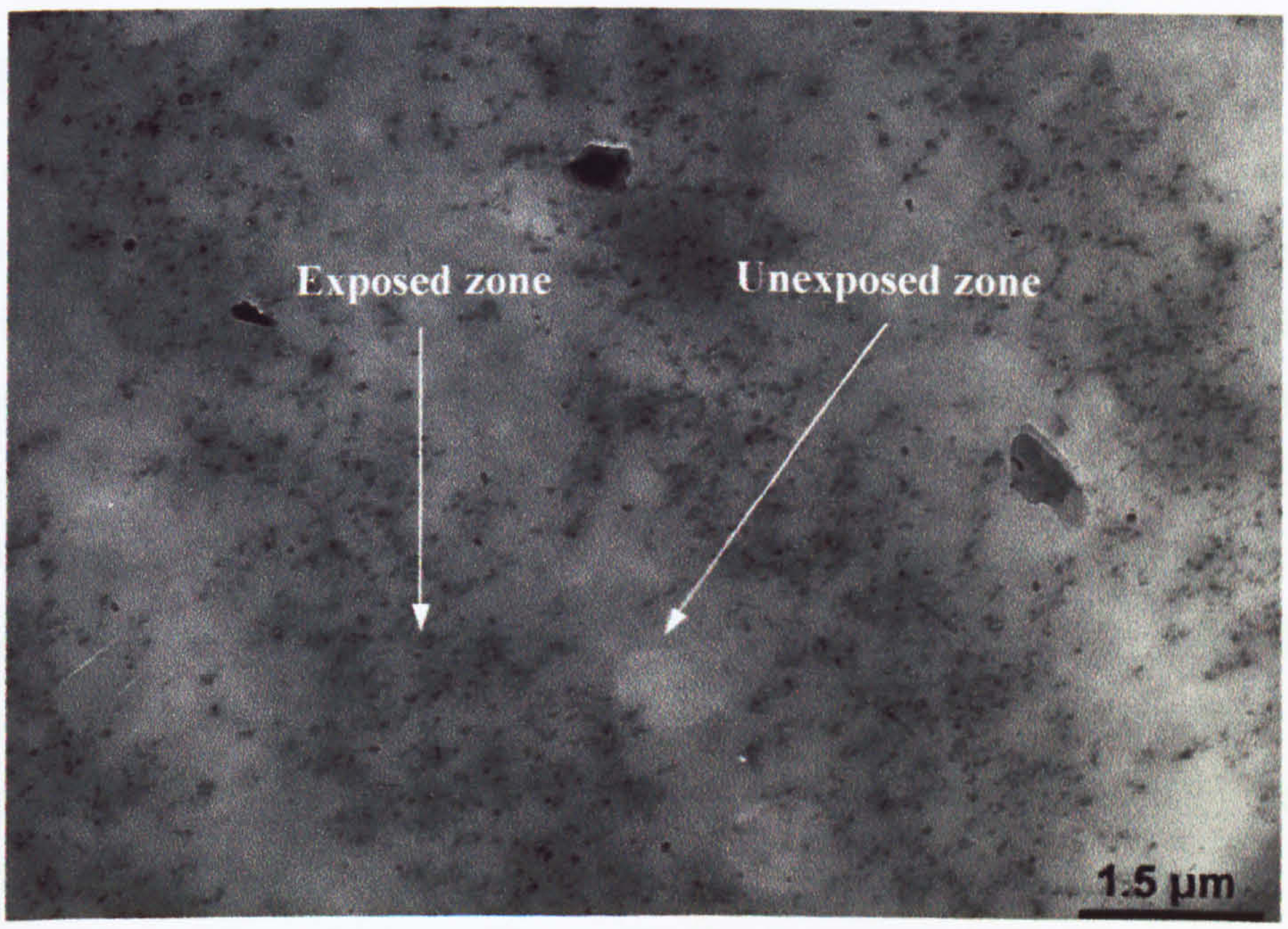

Fig. 2. 7 Cross-sectional TEM image of SHSG processed VR-P plate (Low magnification, which shows the fringes in the emulsion)

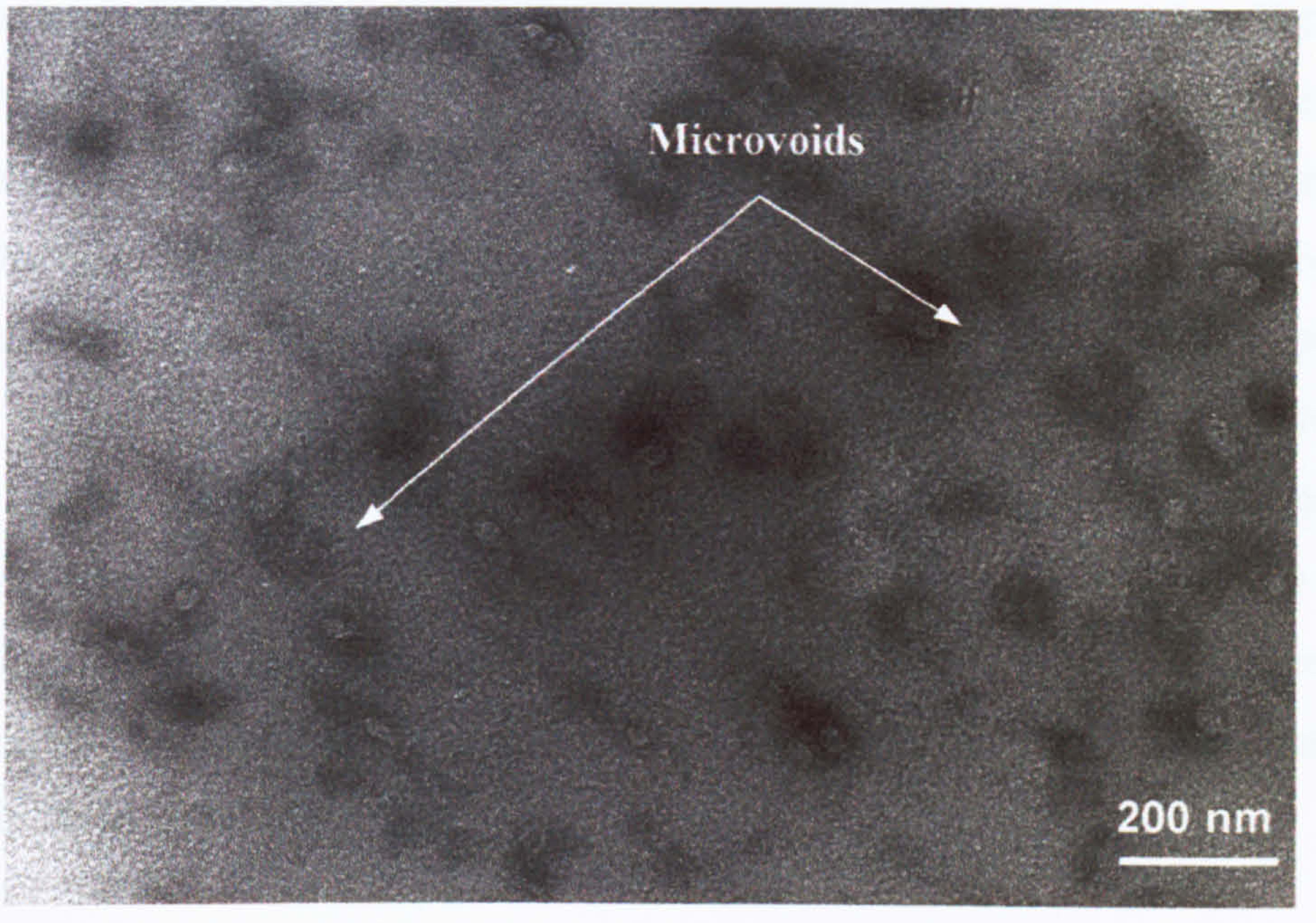

Fig. 2. 8 Cross-sectional TEM image of SHSG processed VR-P plate (High magnification, which shows the microvoids in the emulsion)

2.7 Improved SHSG Wet Processing for Transmission HOEs

Various developing, bleaching and fixing baths have been tested in order to find out the maximum DE using VR-P, PFG-03C and Millimask materials. First, the difference between two non-tanning developers, the AAC developer and the lithographic Agfa G282c developer, were investigated. The optical density of the plates developed in the AAC developer is slightly higher than that of the plates developed in G282c. The results obtained from both developers were almost same. For the practical SHSG process, it may be beneficial to use a standard developer, such as G282c (the developer for high speed reversal processing of Agfa Millimask plates) since the consistency of materials used in mass production is essential for the reproducibility of products. Such non-tanning developers usually contain halide solvents and encourage sharp developed image edges. In addition, they endow the emulsion with a notable speed gain when compared to normal high contrast development.

Another important factor in SHSG processing is how fast silver halide is removed from the emulsion during fixing. When silver salts are removed the microvoids may be affected. The concentrations of the fixing solutions used and its influence on DE have been investigated. Employing weaker fixers means that a longer processing time is needed to remove the silver salts. The slower this process is the less is its potential negative influence on the emulsion microstructure, provided that the selective emulsion hardening is optimal in previous processing steps. To verify that the fixing speed is important, standard fix of different dilutions were tested as well as fixing solutions composed of 10 g/l and 40 g/l sodium thiosulfate (hypo). The processing time in these weak fixing solutions may take ten to twenty minutes to completely remove the silver salts. The influence on DE obtainable on Millimask plates is presented in Fig. 2.6. A concentration of 10 g/l sodium thiosulfate resulted in the highest DE.

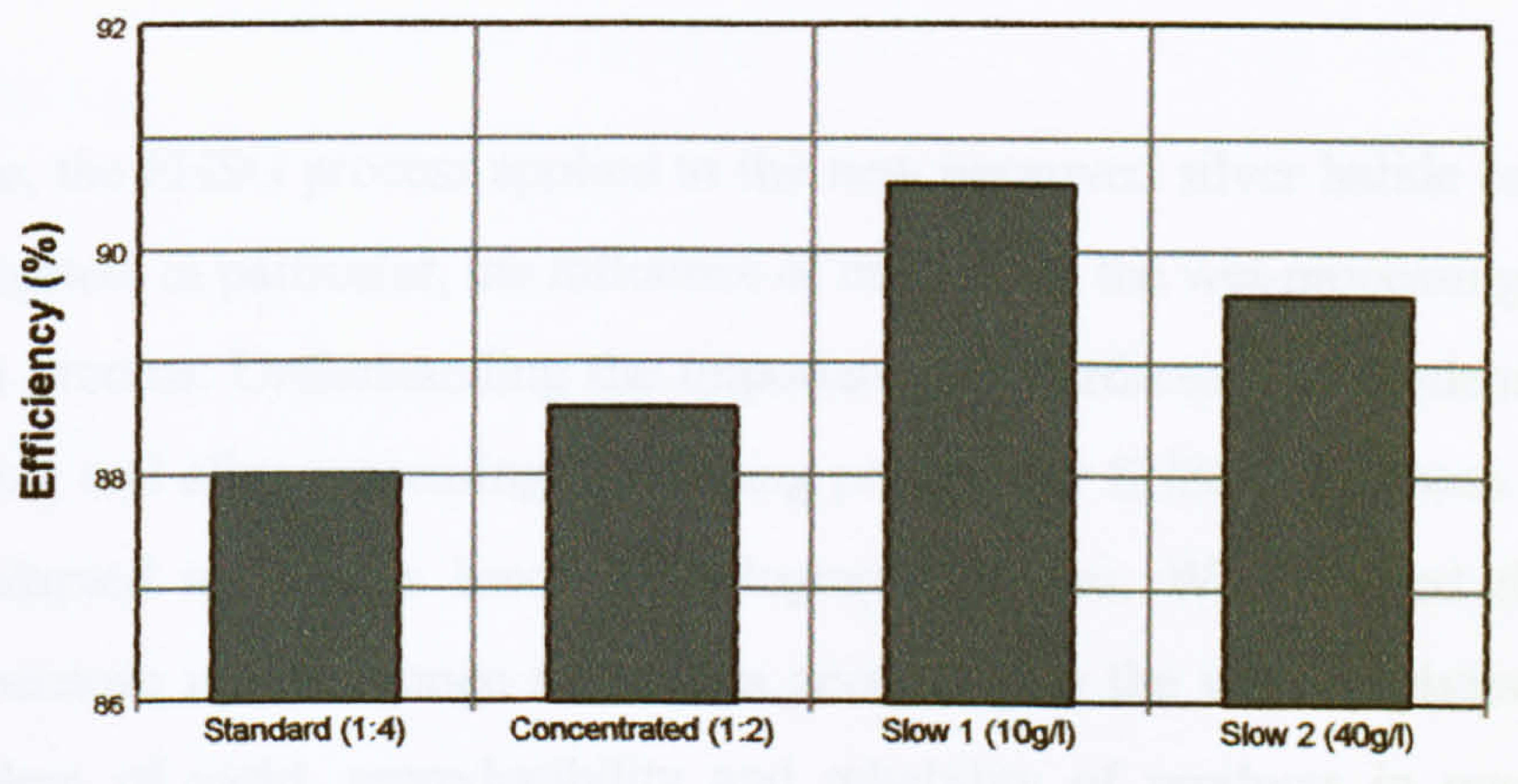

Fig. 2. 9 DE of Millimask plates as a function of fixing solution

The new SHSG processing procedure investigated in this work is summarized in Table 2.2. Transmission HOEs were prepared just in the same way that has described in section 2.4 and DE values were measured with the measuring system shown in Fig. 2.3. The diffraction efficiencies obtained with the new optimized SHSG process are presented in Fig. 2.7.

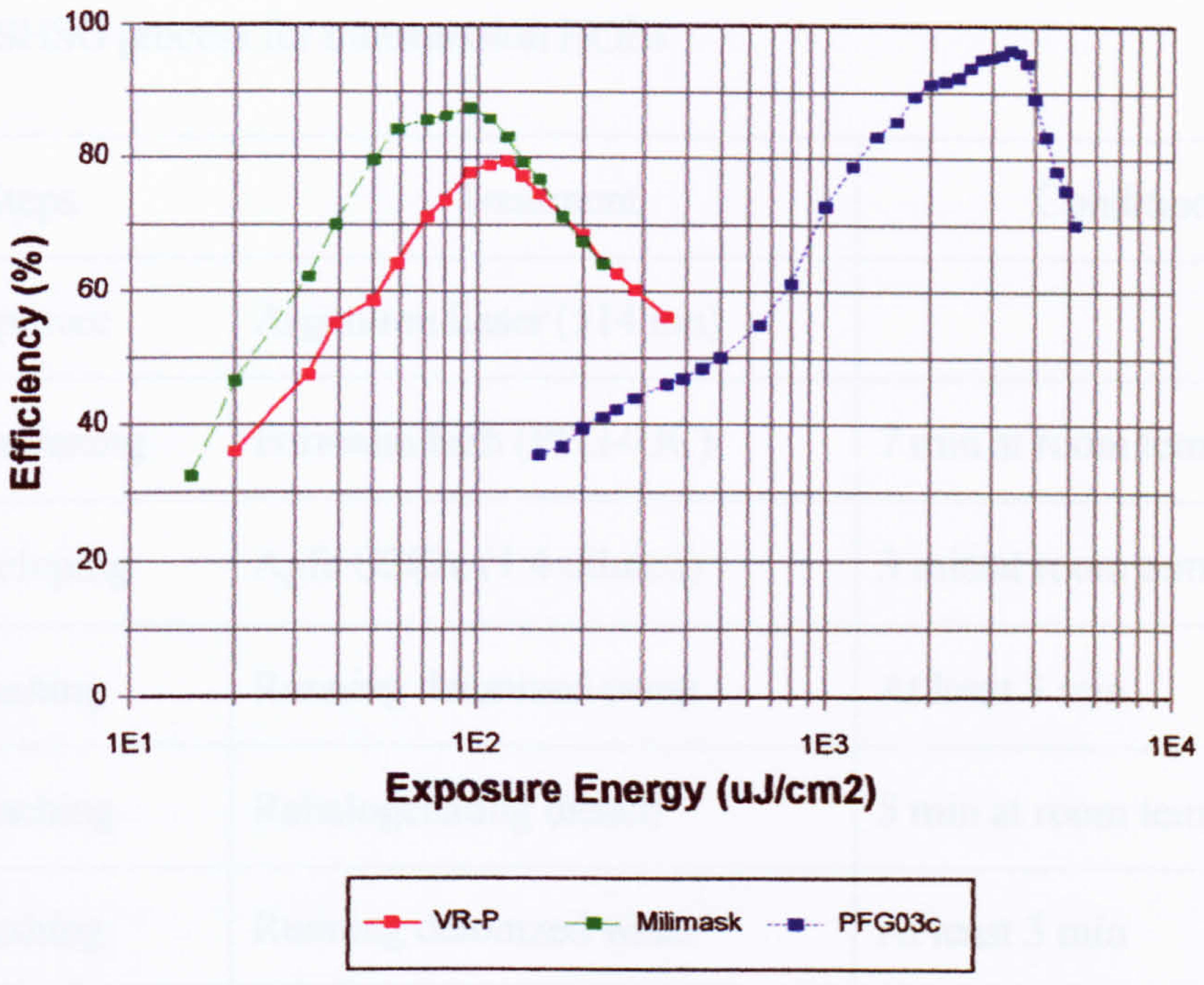

Fig. 2. 10 Efficiency of transmission grating processed with the SHSG method

To conclude, the SHSG process applied to the new improved silver halide emulsions have been investigated, in particular, the influence of hardening, the wet-processing steps and the dehydration process. Understanding the importance of hardness and hardening procedure before, during and after processing, a working process for SHSG have been found, which could be adapted to various kinds of holographic plates. We believed that it is very important because minor change in process according to the various plates will cause a major problem of yield, reproducibility and reliability of products in mass production situation.

In addition to the Slavich emulsions used in this investigation, there are two red sensitive emulsions, the PFG-03M emulsion and the PFG-01. The PFG-03M is of the ultra-high resolution type and similar to the PFG-03C material. The faster PFG-01 emulsion can be used for SHSG processing of transmission HOEs recorded with red laser wavelengths. The new silver halide emulsions are most suitable for recording high-efficiency transmission HOEs using SHSG processing. Similar results were reported in the investigation of the German HRT BB-640 emulsion by Neipp *et al.* [2.6]

Table 2. 2 SHSG process for transmission HOEs

Steps	Treatment	Condition
Exposure	Argon-ion Laser (514 nm)	
Prehardening	Formalin bath (PFG-03C)	7 min at room temperature
Developing	Agfa G282c (1:4 diluted)	3 min at room temperature
Washing	Running deionized water	At least 3 min
Bleaching	Rehalogenating bleach	5 min at room temperature
Washing	Running deionized water	At least 3 min
Fixing	Diluted fixer	3 min at room temperature
Washing	Running deionized water Hot deionized water	At least 3 min 10 min at 45~70°C
Drying	50%: 50%, (Isopropanol: deionized water) 100% isopropanol 100% isopropanol	3 min at 30°C 3 min at 30°C 2 min at <75°C

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Chapter 3

Reflection HOEs Recorded in SHSG Emulsions

3.1 Introduction

It has been difficult to make SHSG processed HOEs of the reflection type because much higher spatial frequencies are recorded in the reflection holograms than in HOEs of the transmission type. In the previous chapter, the theory of SHSG processing has been discussed. In addition, a new processing regime to make transmission HOEs possessing high diffraction efficiency has been introduced. In the transmission case different types of commercial AgHal material such as Agfa, Kodak, or Ilford holographic materials can be used. Up until now most of the SHSG techniques have been developed for such materials and only performed well for transmission HOEs. The possibility of applying SHSG processing to the case of reflection HOEs in the past, using existing Agfa, Kodak, or Ilford AgHal materials, has been limited. When SHSG processing methods have been attempted for reflection HOEs recorded in such materials, obtainable DE (diffraction efficiency) has been limited to approximately 55%. [3.1]

As a matter of fact, SHSG techniques for reflection HOEs have been developed by Russian scientists having access to domestic ultra-fine-grain AgHal emulsions over many years. A remarkable Russian research programme in this field was undertaken by Usanov *et al.* [3.2-4]. Their work has been described in Chapter 1. One important point emphasized in their work is that the material needs additional hardening before the fixing step. After that, it is dehydrated using graded isopropanol solutions similar to conventional DCG processing.

Transmission HOEs are easier to record and process than HOEs of the reflection type because of the structural difference of the fringe patterns. The fringe patterns of reflection HOEs are multi-layered structures which are parallel to the emulsion surface but those of transmission HOEs are single-layered and perpendicular to the emulsion surface. Since there are vacancies, that is, microvoids or empty spaces between the fringes in the reflection HOEs, it is very difficult to maintain the multi-layered structure. In other words, the multi-layered structure is fragile and may collapse during and after processing. Because of these reasons, the process of Chapter 2 when applied to reflection HOEs did not yield satisfactory results. To obtain high quality reflection HOEs in such materials, a new processing regime and a more complicated process had to be developed. For such HOEs only the new ultrafine-grain emulsions can be considered. In fact, only less light sensitive AgHal emulsions are worthy of consideration.

In this Chapter, the recording and processing of reflection HOEs recorded in ultra-fine-grain emulsions are described. The basic process is almost same as for transmission: only the details are different. Instead of rehalogenating dichromated bleaching, normal rehalogenating bleaching solution has been used and some modifications have been made to enhance the hardening action in the emulsion. The microstructure of the emulsion processed with the new reflection SHSG process has been investigated using SEM (scanning electron microscopy). The changes in the size of microvoids according to the conditions of process are clearly visible in the SEM photograph.

3.2 AgHal Materials for Reflection SHSG

The AgHal grain size of the recent material like Agfa Holotest emulsion is too large to be suitable for manufacturing reflection HOEs. After Holographic Recording Technologies GmbH in Germany announced that all holographic materials, e.g., BB-640 [3.5], will no longer be manufactured, the only commercial materials available on the market are for the present the Slavich AgHal materials. Here, mainly their ultra-fine-grain AgHal materials have been considered, such as, Slavich PFG-03M and PFG-03C [3.6]. The PFG-03M is a red sensitive emulsion and PFG-03C is of the panchromatic type sensitized over the entire visible spectrum and, thus, suitable for recording color reflection HOEs. The main differences between Slavich and former Agfa holographic materials are the grain size and the silver content in the emulsion. The panchromatic Slavich emulsions have grain sizes as small as 10 nm. The former highest quality Agfa materials (Holotest HD materials) had grain sizes of approximately 45 nm. The Slavich silver content that was lower than the silver content in Agfa materials has now been improved and is approximately 3.2 g/m^2. Since the resolving power of the AgHal emulsion for recording holograms and HOEs of the reflection type has to be very high, currently, only the Slavich emulsions mentioned above could meet the requirements. This is, in particular true when blue laser wavelengths are used for the recording. If λ is the wavelength of the laser light used for the recording of a hologram, then the closest separation Λ_a between the fringes in the interference pattern (in air) is

$$\Lambda_a = \frac{\lambda}{2\sin(\theta/2)} \tag{3-1}$$

where, θ is half of the angle between the recording reference and object beams. In the recording layer the fringe spacing Λ_e will depend on the refractive index n of the emulsion and is

$$\Lambda_e = \frac{\lambda}{2n\cdot\sin(\theta/2)} \tag{3-2}$$

Kostuk and Goodman measured the refractive index of a holographic AgHal emulsion (Agfa 8E75HD.) They found the following values: unprocessed emulsion (gelatin containing AgHal), n = 1.64; fixed emulsion (pure gelatin), n = 1.54; and fixation-free rehalogenated emulsion, n = 1.64. All refractive indices were measured at the wavelength of yellow D lines of sodium spectrum (λ=589.2 nm). [3.7] For a reflection HOE recorded in blue light (λ = 400 nm) with an angle of 180° between the beams in a AgHal emulsion with a refractive index of n = 1.64, a resolving power of approximately 8200 lines/mm is needed. However, this is the minimum resolving power required. Close to its resolution limit, the material will exhibit a low modulation transfer function (MTF) and will thus make a low-quality hologram with poor fringe contrast and low signal-to-noise ratio.

Even if the resolving power of a particular emulsion is just able to resolve the recorded interference fringes, the quality of the recorded HOE may be poor because of Rayleigh scattering that occurs during the recording. Light scattering off AgHal crystals in the emulsion is proportional to the sixth power of their radius for a given wavelength. There is also an increase in scattering with the inverse fourth power of the wavelength as wavelength decreases. The importance of these considerations was treated in great detail in Chapter 2. The reason why HOEs are recorded in traditional materials, such as, e.g., DCG and photopolymer materials, is that these materials have high resolving power combined with low Rayleigh scattering during recording. However, the new ultra-fine-grain AgHal materials have similar performance combined with the additional advantages of high energetic sensitivity and full panchromatic response.

As pointed out by Fimia *et al.*, [3.8] SHSG processed HOEs have the same spatial frequency response as the photographic emulsion used at the outset. This makes it difficult to obtain high DE when the spatial frequency is high, using coarse-grain AgHal materials. This means, that, so far, it has been difficult to obtain reflection HOEs employing SHSG processing, which could compete in quality and DE with HOEs recorded in DCG or photopolymer materials. Beléndez *et al.* [3.9] compared both theoretically and experimentally the rapid fall in DE as a function of AgHal grain size. The essential cause of the rapid fall observed with Agfa plates as the spatial frequency increased above a critical value is due to the MTF of the photographic emulsion which falls rapidly at high spatial frequencies when the grain size of the of the emulsion is large. Ferrante [3.10] studied the spatial frequency response for Agfa 8E75HD material and concluded that this material can only be used for transmission HOEs up to a certain spatial frequency. More recently, Beléndez *et al.* [3.9] found that an increased spatial frequency response was obtained for the fine-grain BB-640 material due to its smaller AgHal grains (approximately 25 nm) compared with the processed Agfa 8E75HD emulsion grain size (approximately 65 nm). The experimentally obtained results were in good agreement with Buschmann's weakly scattering model [3.11] for grain sizes 25 and 65 nm. The obtainable DE at a spatial frequency of 3000 lines/mm is about twice as high for the 25 nm BB-640 emulsion as compared with the Agfa 65 nm emulsion. It is also important to mention that spatial frequency response of AgHal emulsions for SHSG processing is partly affected by the fact that an enlarged shell of hardened cross-linked gelatin around exposed AgHal grains is created during the hardening action of the bleaching process. Considering all these facts it is obvious that only AgHal materials containing the smallest possible AgHal grains should be considered for obtaining reflection HOEs applying the SHSG processing technique.

3.3 Materials Used in Reflection SHSG

The ultra-fine-grain red sensitive Slavich PFG-03M emulsion and the panchromatic Slavich PFG-03C emulsion were used in this research project. Some characteristics of the Slavich PFG-03C material are presented in Table 3. 1. Fig 3.1 shows that the grain size of these emulsions lies between 5 and 15 nm. [3.7] There is no antihalation coating since the materials are intended for the recording of both transmission and reflection holograms. The PFG-03C emulsion was the preferred material for most of the tests to use red, green, and, in particular, blue laser wavelengths.

Table 3. 1 Characteristics of the PFG-03 emulsion and grain size distribution.

Property	Value
Silver halide material	PFG-03C
Emulsion thickness	7 μm
Grain size	10 - 20 nm
Resolution	~10000 lp/mm
Blue sensitivity	~1.0 - $1.5 \cdot 10^{-3}$ J/cm^2
Green sensitivity	~1.2 - $1.6 \cdot 10^{-3}$ J/cm^2
Red sensitivity	~0.8 - $1.2 \cdot 10^{-3}$ J/cm^2
Colour sensitivity peaked	At 633 nm, 530 nm, 450 nm

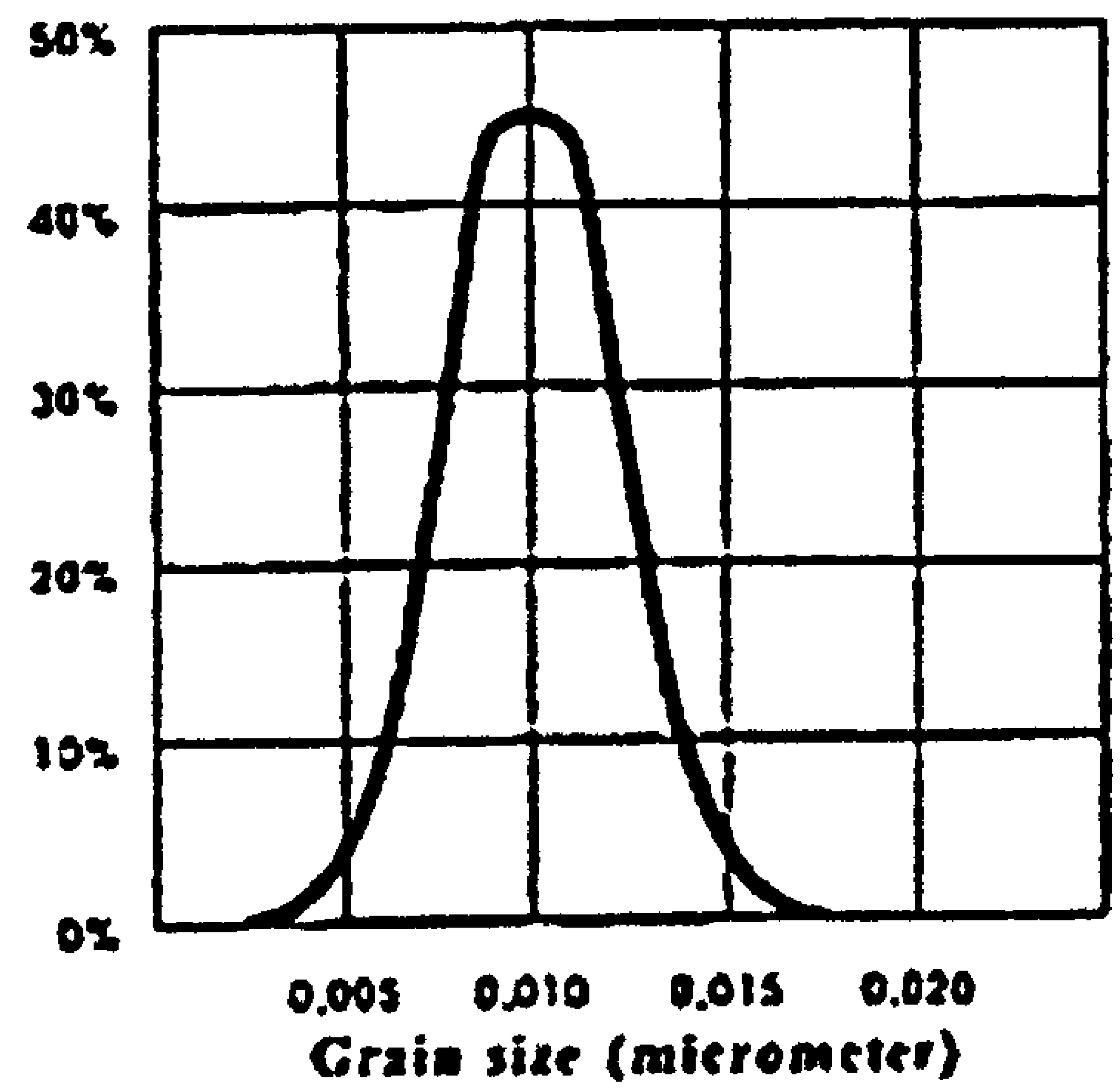

Fig. 3. 1 Grain size distribution for the PFG-03M Material. [3.7]

3.4 Gelatin Hardening and its Role in SHSG Processing

Emulsion characteristics, emulsion hardening in general and the selective hardening for producing SHSG holograms were treated in previous chapter. If too soft, prehardening before development is necessary. If such prehardening is not performed, the microvoids formed in the gelatin structure will collapse or be destroyed. On the contrary, if the emulsion is too hard, the amplification of microvoids does not occur during the drying process. Given this fact, it is important to understand fully the behavior of the AgHal emulsion and its response to hardening procedures.

So far, in previous SHSG processing, mainly dichromate bleaches of the Kodak R-10 type have been used. However, when dealing with high spatial frequencies such as the case in processing reflection HOEs, the dichromate bleach is not recommended because of its tendency to produce large rehalogenated grains and yellow emulsion stain. However, the stain can be removed, but during the stain removal process, the hardening of the emulsion may be adversely affected.

Already in a very early publication on SHSG processing, Graver *et al.* [3.12] suggested that, after bleaching, cross-linking could occur only in a subsequent washing bath that has the correct pH for the process to proceed. This important observation seems to have been overlooked since then. Later Fimia *et al.* [3.13] found that, by interrupting the process after the bleaching step (without washing the plate) and leaving the plate in high humidity (90% RH) for 24 hours, improved results caused by increased cross-linking during that time.

Based on these facts, bleaching and selective hardening were split into two processing steps. The first is the bleaching step for which any suitable rehalogenating bleach can be used, provided that a hardening compound is added to the bleach, although this is not very active in the bleaching process. If possible, the bleach should be operating at the isoelectric point in order to avoid excessive swelling. Also the temperature of the bleach should be at approximately 20°C to avoid rehalogenated grains becoming too large. The second bath is a pH 5 water solution, in which the selective cross-linking process will take place. This process can be greatly enhanced by increasing the temperature of this solution. By this approach it is possible to obtain high DE combined with low noise level. The two-step process is much preferred over methods employing hot bleach baths.

For reasons mentioned above, the common Kodak R-10 type chrome bleach is to be avoided. Instead, alternative bleach solutions were considered, which perform better when processing high spatial frequency HOEs. Here, the PBU bleach baths are highly suitable. [3.14] In particular the metol-based bleach (PBU-metol), which bleaches without leaving any stain in the emulsion. Another advantage is that no emulsion shrinkage occurs. The oxidized metol in the bleach may provide some additional hardening. However, a hardening compound has to be added to this bleach. Which compound to select as well as which concentration to use needed extensive investigations and tests.

The capabilities of attacking silver in gelatin layers and hardening of gelatin by chrome and aluminum ions have been studied. Various chemicals, such as, e.g., chromium chloride, aluminum chloride, and aluminum nitrate, were tested as additives in the bleach. The gelatin molecule cross-linking process depends on the number of the Cr^{3+} ions and, in particular, the pH of the bleach solution. The acidic nature of the most common bleach solutions employed in SHSG processing tends to prevent efficient cross-linking to take place during bleaching. Finally, it was decided that between 1% and 3% of chromium (III) potassium sulfate (chrome alum) should be added to the PBU-metol bleach solution. This compound performed best as the provider of Cr^{3+} ions in the bleach, it mixed very well with the other constituents and did not stain the emulsion.

However, most important was the application of a process introduced by Usanov and Shevtsov. [3.4] After the two-step bleaches and selective hardening process is completed, additional emulsion surface hardening is required, otherwise the microvoids should be burst away during the final drying step, which destroys the whole structure in the emulsion and results in whitening or fogging up the HOEs. This process can be performed by drying the emulsion in ethanol and then exposing the dry emulsion to formaldehyde vapor in a heated sealed container, a technique introduced by Usanov. [3.15] In this case the hardening process can be performed in fifteen to thirty minutes. What is important here is the extensive hardening of the emulsion surface that occurs during the dry hardening step. The hard surface allows high vapor pressure to build up inside the microcavities during the final dehydration step. Under this pressure, the microvoids expand and isopropanol is replaced by air, thus providing the high refractive index variations in the emulsion.

To avoid emulsion shrinkage the amount and size of the microvoids need to be accurately controlled throughout the processing (it is noted that excessive number of microvoids will lead to a whitening of the gelatin which is created by bursting of microvoids at the emulsion surface, a phenomenon also observed with incorrectly hardened DCG).

3.5 SHSG Processing for Reflection HOEs

Various developers, bleaching - and fixing baths have been tested in order to find the maximum obtainable DE of HOEs in Slavich emulsions. The development step is important and selecting the best developer needed some tests. However, as regards the ultra-fine-grain emulsions, the developer is less critical as compared to processing coarse-grain materials where the size and shape of the developed silver grains in the emulsion very much depend on the developer. In principle, we have tanning and nontanning developers to consider. Normally, nontanning developers are preferred for SHSG processing. Tanned (hardened) gelatin formed in developing bath may reduce the action of enlargement caused by rehalogenation. The nontanning ascorbic-acid-based AAC developer does not generate any oxidation products during development and was proven to work fine with the former Agfa holographic materials. [3.13] Oxidation products produced during development can influence the rate of development. [3.16]

The following developers have been tested: AAC, CW-C2, Kodak D-19 and Agfa G282c. In the work done by Neipp *et al.* [3.17] on the influence of the developer type for processing the Slavich PFG-01 material, they found that the Agfa 80 developer worked very well. Agfa 80 is a metol quinol (MQ) developer with large amount of sodium sulfite to prevent tanning. Another Agfa developer is the lithographic G282c developer (the developer for high speed reversal processing of Agfa Millimask plates.) Such nontanning developers usually contain halide solvents and encourage sharp developed image edges. In addition, G282c actually endows the emulsion with a notable speed gain when compared to normal high contrast development. This developer gave the best results in the new SHSG processing scheme.

The bleaching process was carefully investigated. The new bleach was based on the rehalogenating PBU-metol bleach [3.14] and the modified version is mixed in the following way (stock solution):

Cupric bromide	1	g
Potassium persulfate	10	g
Citric acid	50	g
Potassium bromide	20	g
Borax	30	g
Deionized water	1	l.

1 g metol (*p*-methylaminophenol sulfate) is added after the other constituents are mixed. In order to make this bleach operate at a pH of approximately 5, Borax (sodium tetraborate, decahydrate) was added in order to obtain the optimal condition for SHSG processing. A hardening compound needed to be added as well. After conducting many experiment, Cr^{3+} ions were introduced in this bleach by adding 2% chromium (III) potassium sulfate to the bleach. The new SHSG process is illustrated and the main processing steps are summarized in Table 3.2.

Table 3. 2 Main SHSG processing steps

No	Processing steps	Time
1	Prehardening in a Formaldehyde solution	6 min
2	Develop in Agfa G282c developer @22°C	3 min
3	Bleach in the PBU-metol SHSG bleach (diluted 1:3)	3. ~15 min
4	Treat in warm deionized water @60°C	10 min
5	Dehydration in: 50% water/50% IMS 100% IMS	3 min 3 min
6	Dry in oven @45°C	5 min
7	Harden in the chamber with formaldehyde vapor	15 min
8	Fix in SHSG fixing solution	2 min
9	Wash in the deionized water @40 ~ 60°C	5 min
10	Dehydrate in: 50% water/50% IPA 100% IPA @20°C 100% IPA @70°C	10 min 10 min 2 min

The Agfa G282c developer was selected, because it provided the best results. It is supplied in liquid form and convenient to use. After the development step it is important to use a stop bath (2% acetic acid solution) before bleaching.

In many publications on SHSG processing, warm bleach baths are often used. [3.18-21] In general, a higher DE can be obtained by using a warm (up to 60°C) bleach bath. However, the noise (light scattering) is increased as well. The reason for this is that during bleaching in a warm solution the AgHal grains are increased too much, in particular, when using a R-10 type of bleach. To avoid large rehalogenated grains in new process, the bleaching is performed at room temperature (approximately 22°C) employing the modified PBU-metol bleach, followed by a warm water bath to enhance the selective hardening of the emulsion. To dry the emulsion before the vapor-hardening step, industrial methylated spirit (IMS) instead of ethanol has been used to obtain better color control of the finished result. Since the fixing step needs to be performed in an aqueous solution, which may soften and swell the emulsion too much, a special weak fix solution was formulated. To minimize emulsion swelling sodium sulfate was added as an anti-swelling agent. Ammonium thiosulfate was selected since it has a stronger solvent action on fine AgHal grains than sodium thiosulfate has.

The final dehydration steps are performed in the usual way employing graded isopropanol. The last 100% isopropanol bath is at a temperature of 70°C. To prevent moisture to reach the emulsion the HOEs are sealed with a material which is totally unaffected by water. Several materials such as industrial adhesives (PASCO*FIX*® [3.22]) and UV curable bond have been examined to seal the SHSG processed HOEs. PASCO*FIX*® is based on an alpha-cyanoacrylate ester and contains no solvent. This product is totally unaffected by water. It needs no mixing or UV curing and is applied at room temperature. Normal UV bond can be usable for the sealing of the SHSG processed HOEs since it does not contain solvent.

3.6 Experimental Results

To demonstrate the results of the new processing technique, different reflection HOEs were recorded at three different laser wavelengths: 647 nm, 532 nm, and 458 nm. The recording method of the HOE is shown in Fig. 3.2, which represents the reflection HOEs can be classified as Lippmann holography. A mirror, index-matched to the emulsion side of a plate, was used. After recording, plates were processed using the SHSG process illustrated in Table 3.2.

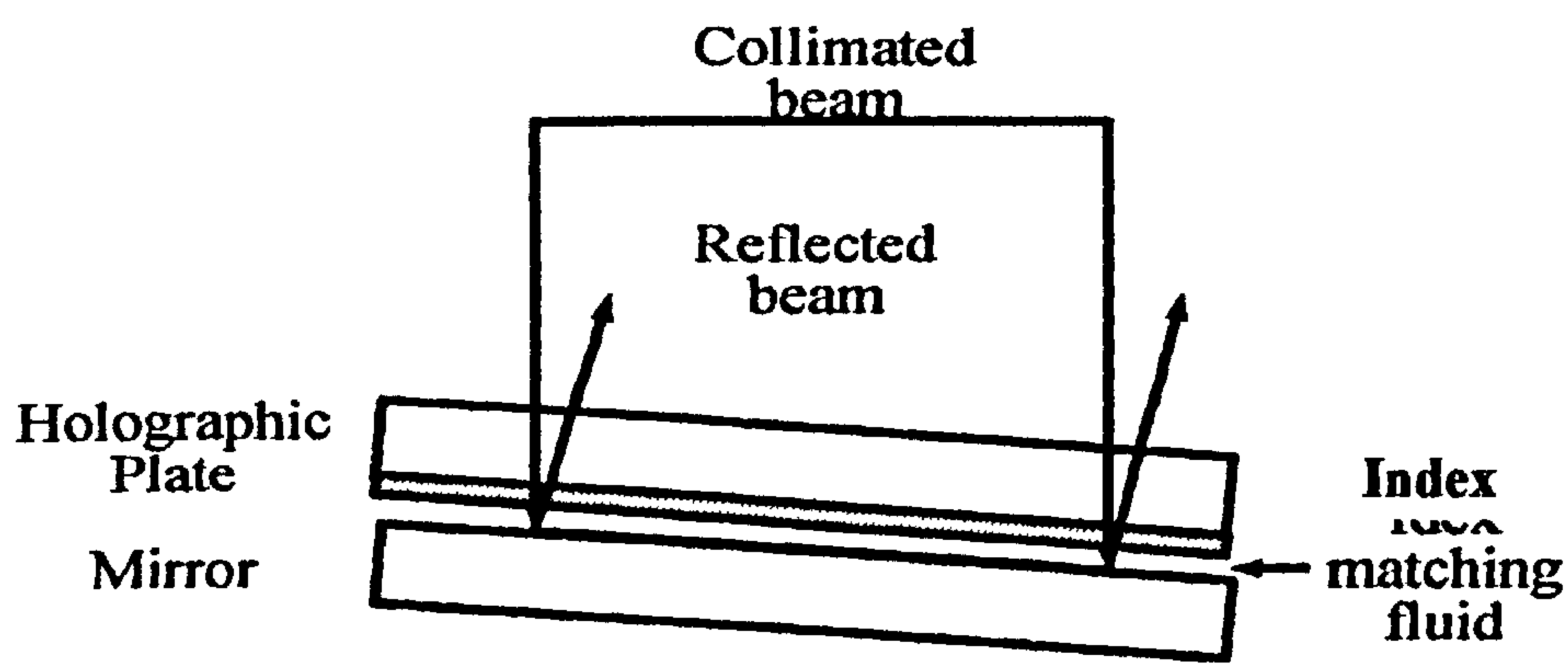

Fig. 3. 2 Optical arrangement for recording and measurement of reflection HOEs

The DE has been measured in two ways; using spectrophotometer from 'Ocean Optics Inc.' [3.23] and goniometric measurement system with lasers, which was described in Chapter 2.

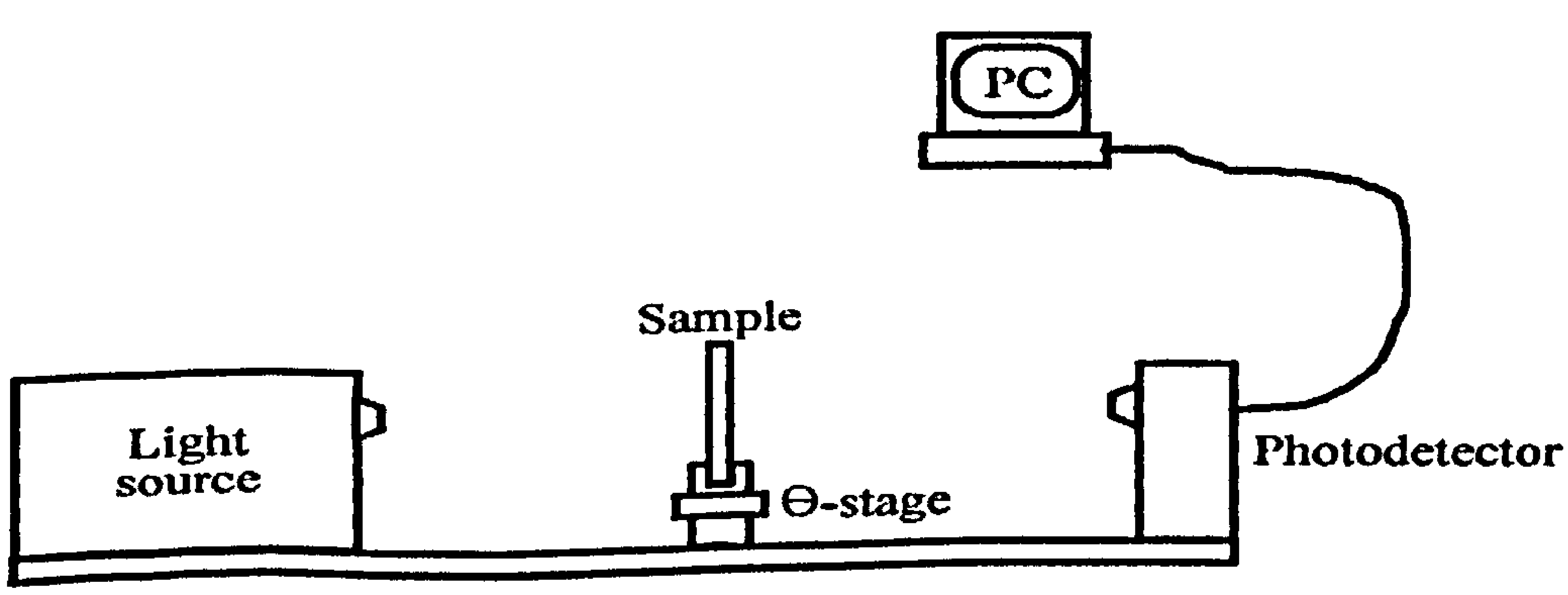

Fig. 3. 3 Schematic diagram of spectrophotometer used for the measurement of transmittance of reflection HOEs

Transmittances of the Lippmann reflection HOEs measured by spectrophotometer are presented in Fig. 3.4. These are three separate recordings in different emulsion samples. DEs of the HOEs are over 96% which include the surface (Fresnel) reflection and exclude absorption by the gelatin layer.

The bandwidths of these recordings are in the order of 20 nm. The bandwidth can be controlled by changing the temperature of the washing bath applied after the fixing. The bandwidths of the HOEs shown in Fig. 3.4 were obtained at the temperature of 50 °C. If we want to increase the bandwidth to, e.g., more than 50 nm, the washing bath should have the temperature of more than 60 °C. The heat treatment in the hot water softens the gelatin to some extent and enhances the hardening procedure in the gelatin mass. Hence heat treatment increases the size of microvoids in both horizontal and vertical direction, which means that fringes recorded in the emulsion get more indistinct and the HOE becomes noisy.

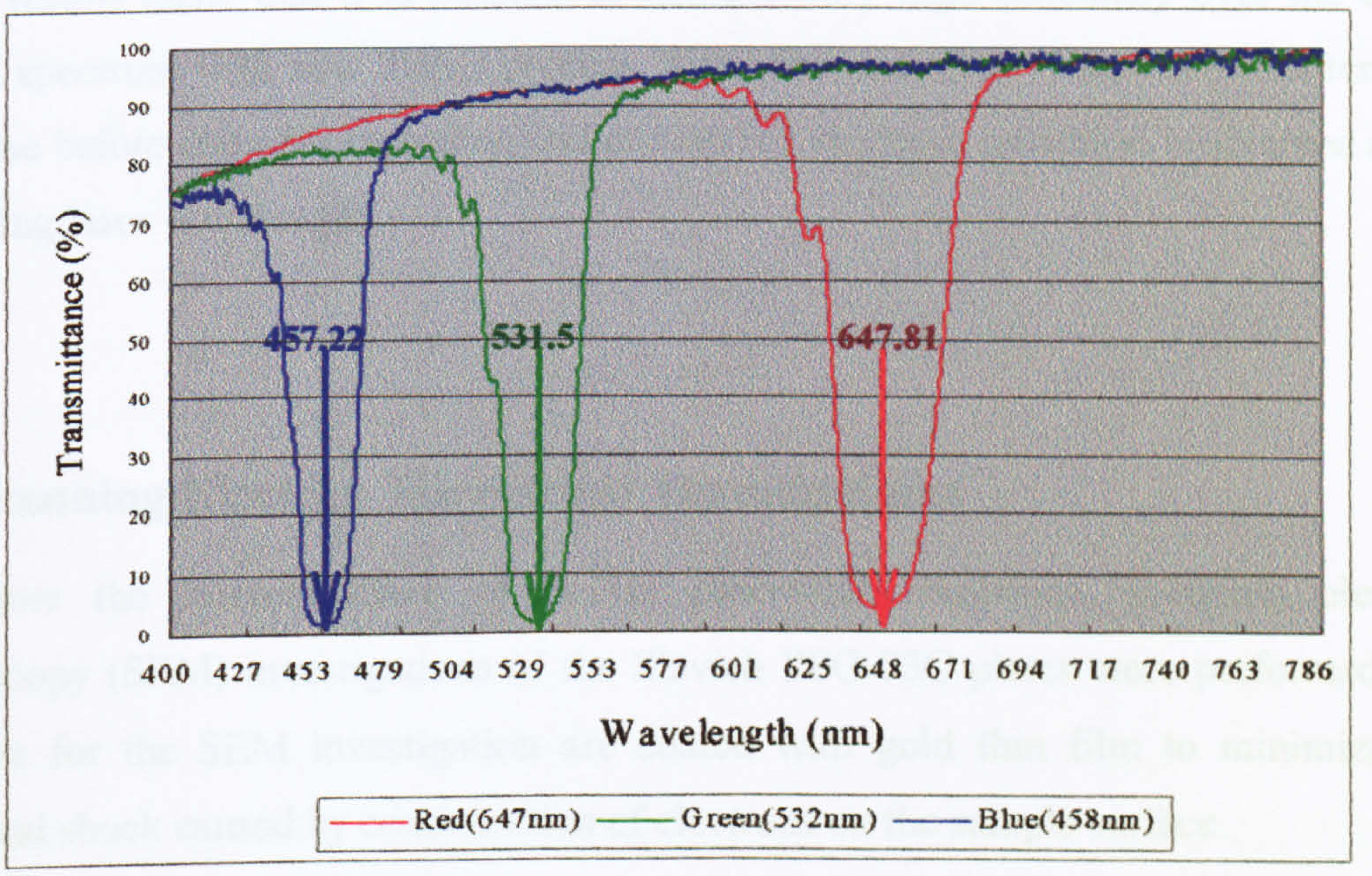

Fig. 3. 4 Transmittance of reflection HOEs recorded in PFG-03c emulsion at three wavelength (λ = 647, 532, 458 nm.)

In Table 3.3, DE measurements of the three samples have been obtained reconstructing the HOEs using the corresponding recording laser wavelengths and precisely controlled goniometric measuring system mentioned in Chapter 2. The results coincide with the transmittance data measured using spectrophotometer.

Table 3. 3 Diffraction efficiency and transmittance of SHSG reflection HOEs measured with the three laser wavelengths used for the recording.

Recording wavelength	Reflection Diffraction Efficiency	Transmittance
458 nm	96.3 %	0.2 %
532 nm	96.5 %	0.5 %
647 nm	96.8 %	0.8 %

These results show that it is possible to achieve very high efficiency over the entire visible spectrum with new SHSG process. Since the thickness of the emulsion remains the same before and after recording and processing, the peak reflection is obtained at the recording laser wavelength.

3.7 Scanning Electron Microscopy Investigations

To show the microstructure of SHSG processed emulsions, scanning electron microscopy (SEM) investigations of the Slavich PFG-03C plates were performed. All samples for the SEM investigation are coated with gold thin film to minimize the electrical shock caused by condensation of electrons on the sample surface

In order to show the importance of sufficient emulsion surface hardening, Fig. 3.5 shows, at 20,000 times magnification, the emulsion surface of a plate, which was not, hardened enough. Bursts of microvoids through the emulsion surface are visible in this figure. From another correctly hardened plate, microvoids located along the interference fringe pattern and propagating through the emulsion, are shown in Fig. 3.6. The entire cross section of the 7 μm emulsion (magnification 6,000X) is shown in this figure. In Fig. 3.7, the same emulsion is shown at higher magnification (20,000X) where the microvoids are visible. At even higher magnification (80,000X) in Fig. 3.8, where only 1 μm of emulsion cross-section is depicted, the microvoids are clearly visible. The SEM investigation of this plate (Fig. 3.7 and 3.8) was a plate that went through the high-temperature (60°C) processing technique.

The size of the voids is approximately up to 100 nm although the average grain size was initially about 10 nm. The enlargement of microvoid size means that the volume density of microvoids increases and consequently total refractive index modulation becomes higher i.e. the DE value gets higher.

The shape and size of microvoids is a very important factor for both DE and bandwidth. The enlargement of microvoids takes place in the horizontal direction, i.e. the direction parallel to the emulsion surface. Thus the shapes of microvoids formed by SHSG process look like oval, as can be easily seen in Fig. 3.8 and Fig. 3.10. If the shape of microvoids is sphere, the recorded fringe will become unclear since they expand during the processing. Accordingly the HOE happens to be broad-banded. The microvoids with elliptical (button-like) shape make the HOEs to have high efficiency and controllable bandwidth (thickness determination of the multi-layered structure).

In Fig. 3.9, (magnification 20,000X) and Fig. 3.10, (magnification 80,000X) the SEM pictures were obtained from a plate processed at a lower temperature (40°C). Here the microvoids are smaller, which means, a more narrow-band behavior. The size of the microvoids in the 1 μm emulsion cross section is approximately 50 nm, as shown in Fig. 3.10.

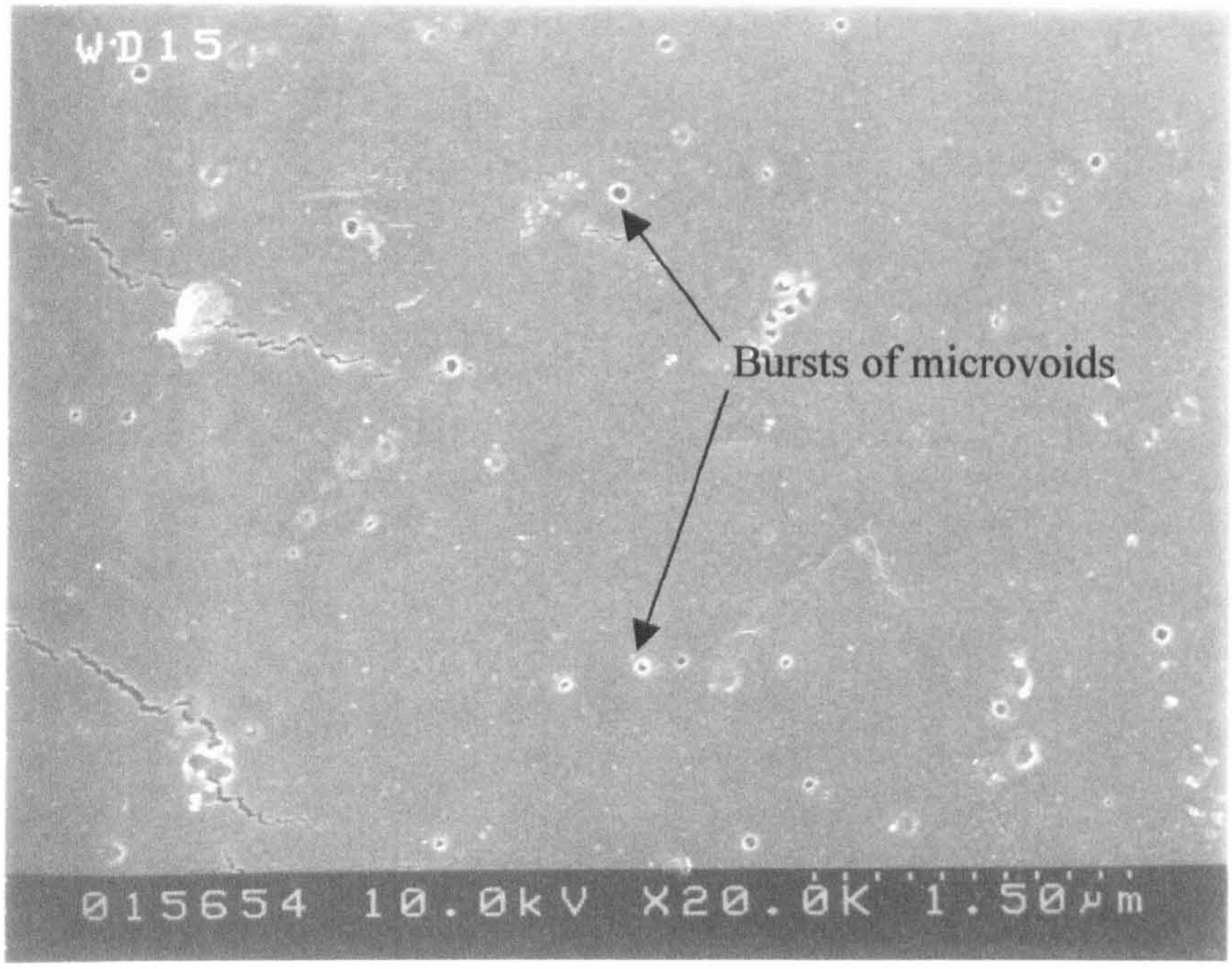

Fig. 3. 5 Air bubbles penetrating in the emulsion surface as a result of insufficient surface hardening. (20,000X)

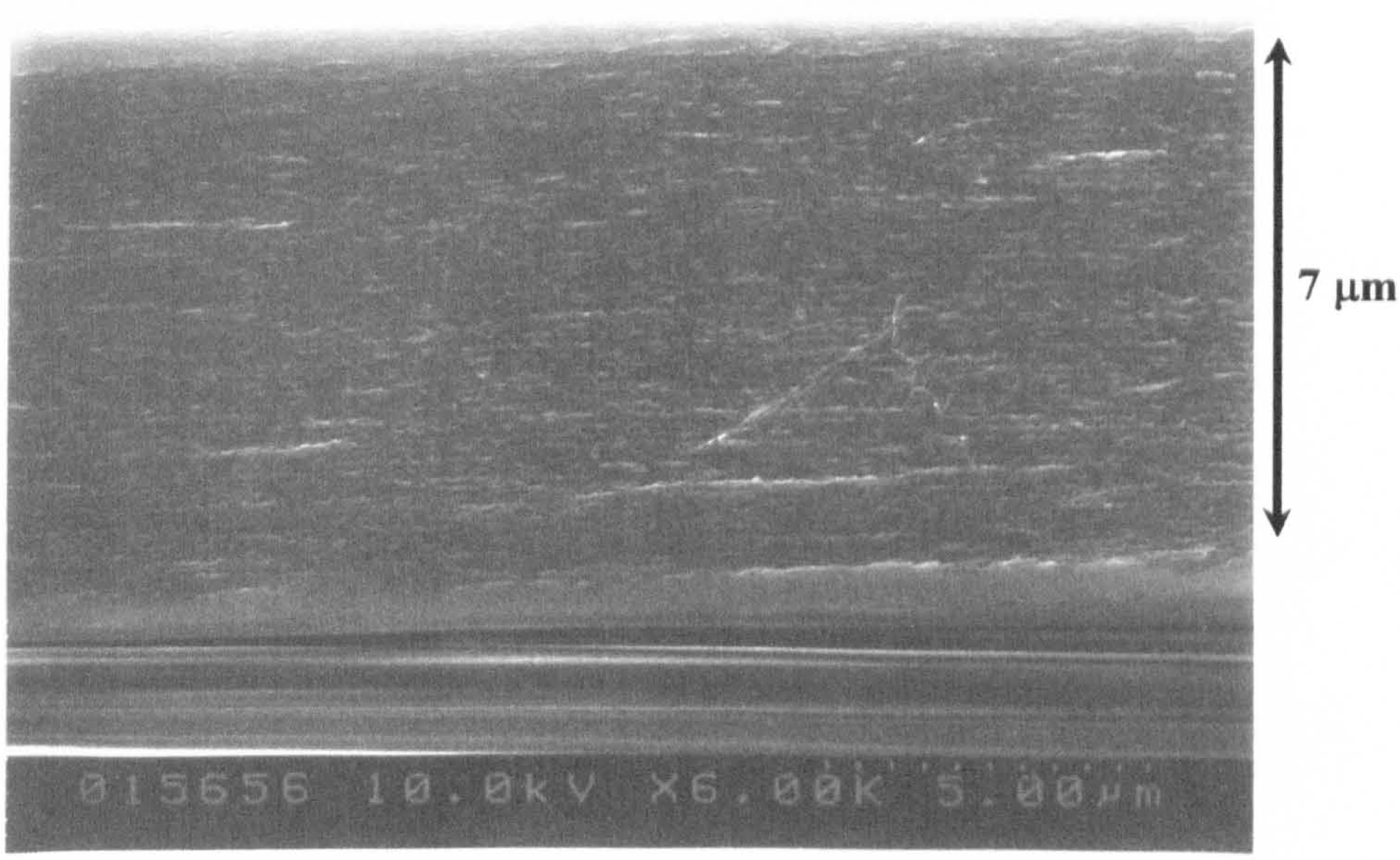

Fig. 3. 6 Microvoids located along the interference fringes in the 7 µm emulsion cross section (6,000X); High temperature processing.

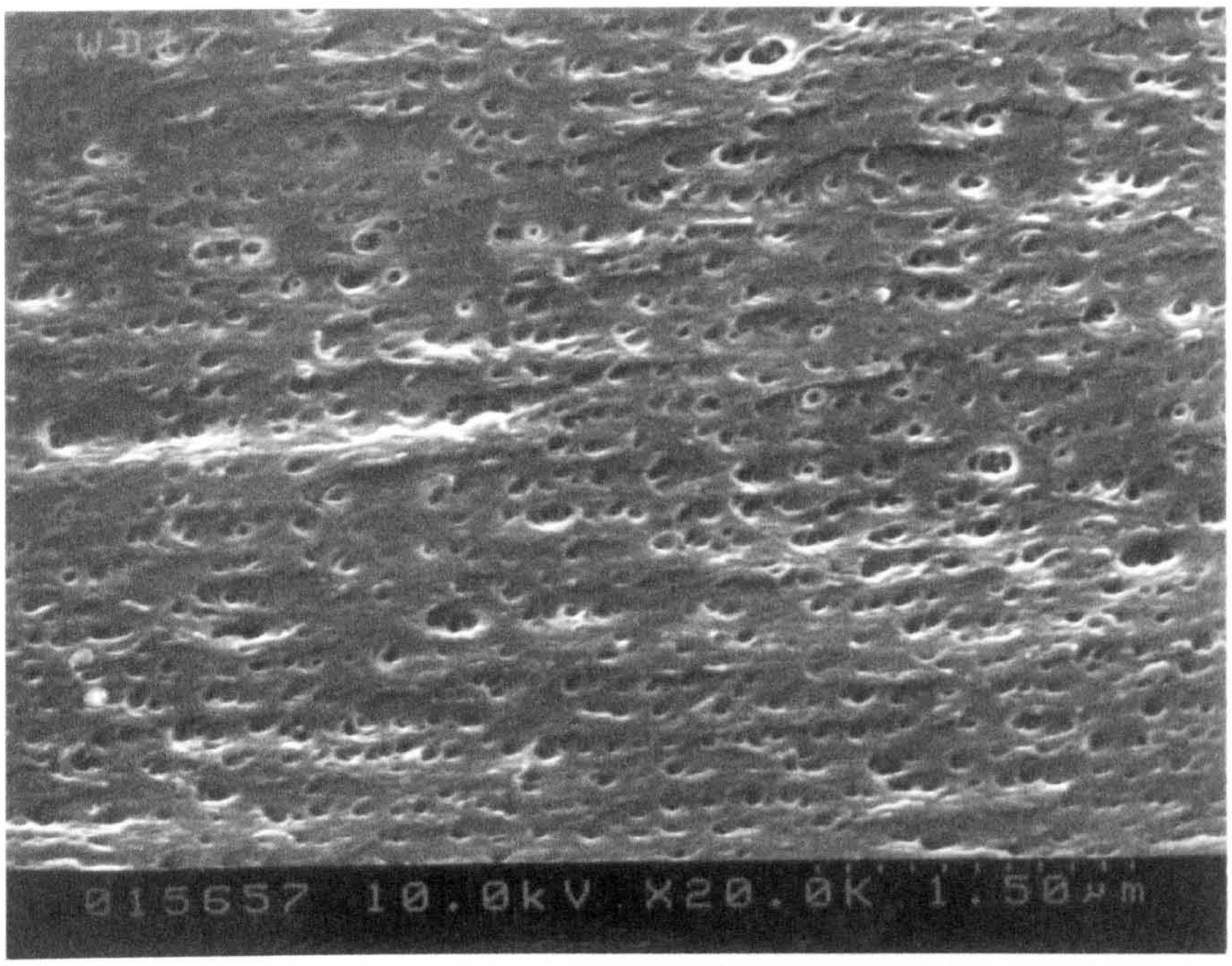

Fig. 3. 7 The same emulsion as in Fig. 3. 5 at high magnification (20,000X). Microvoids are visible here.

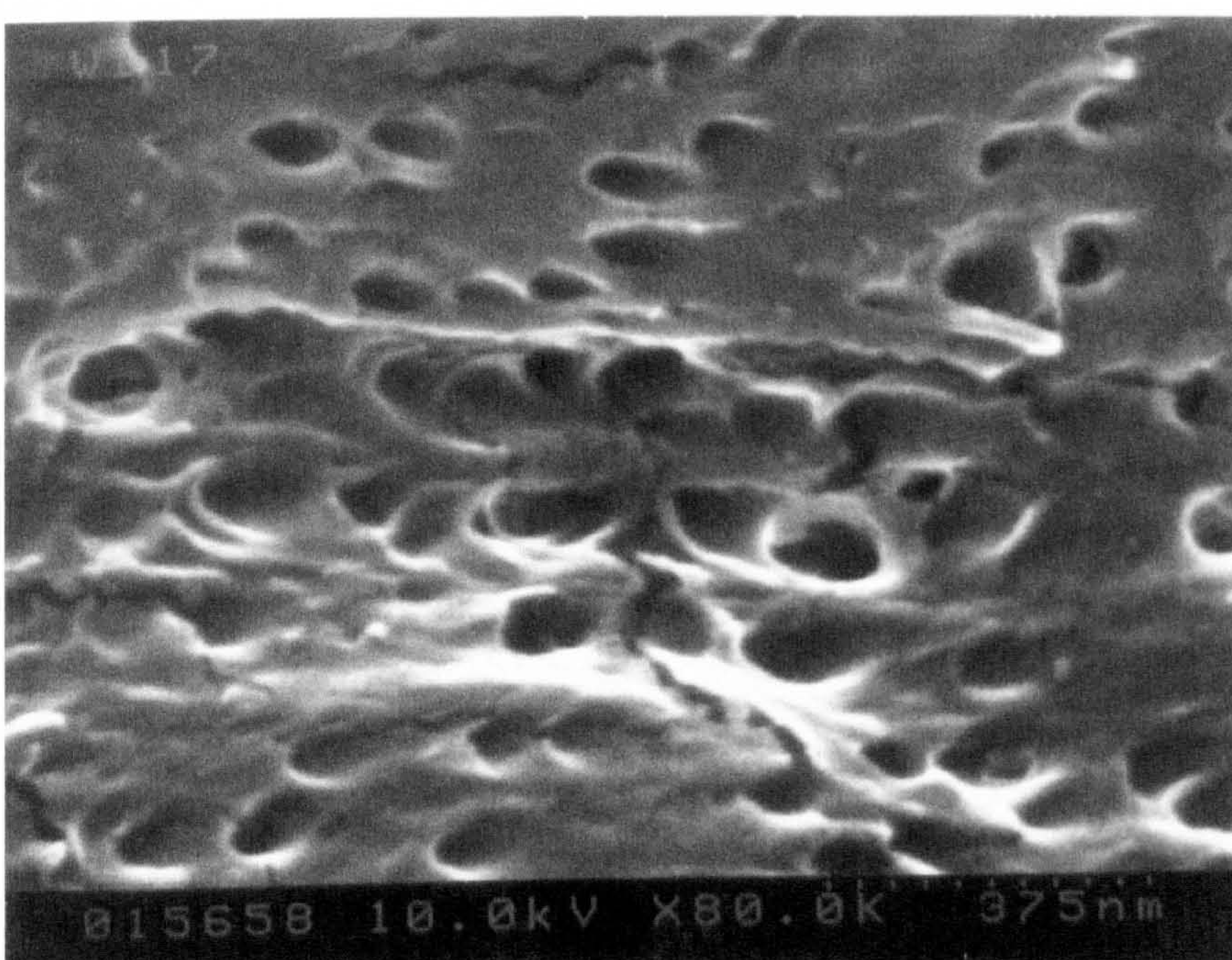

Fig. 3. 8 The same emulsion as in Fig. 3. 5 at higher magnification (80,000X). Microvoids (100 nm) are now clearly visible in 1 μm emulsion cross section.

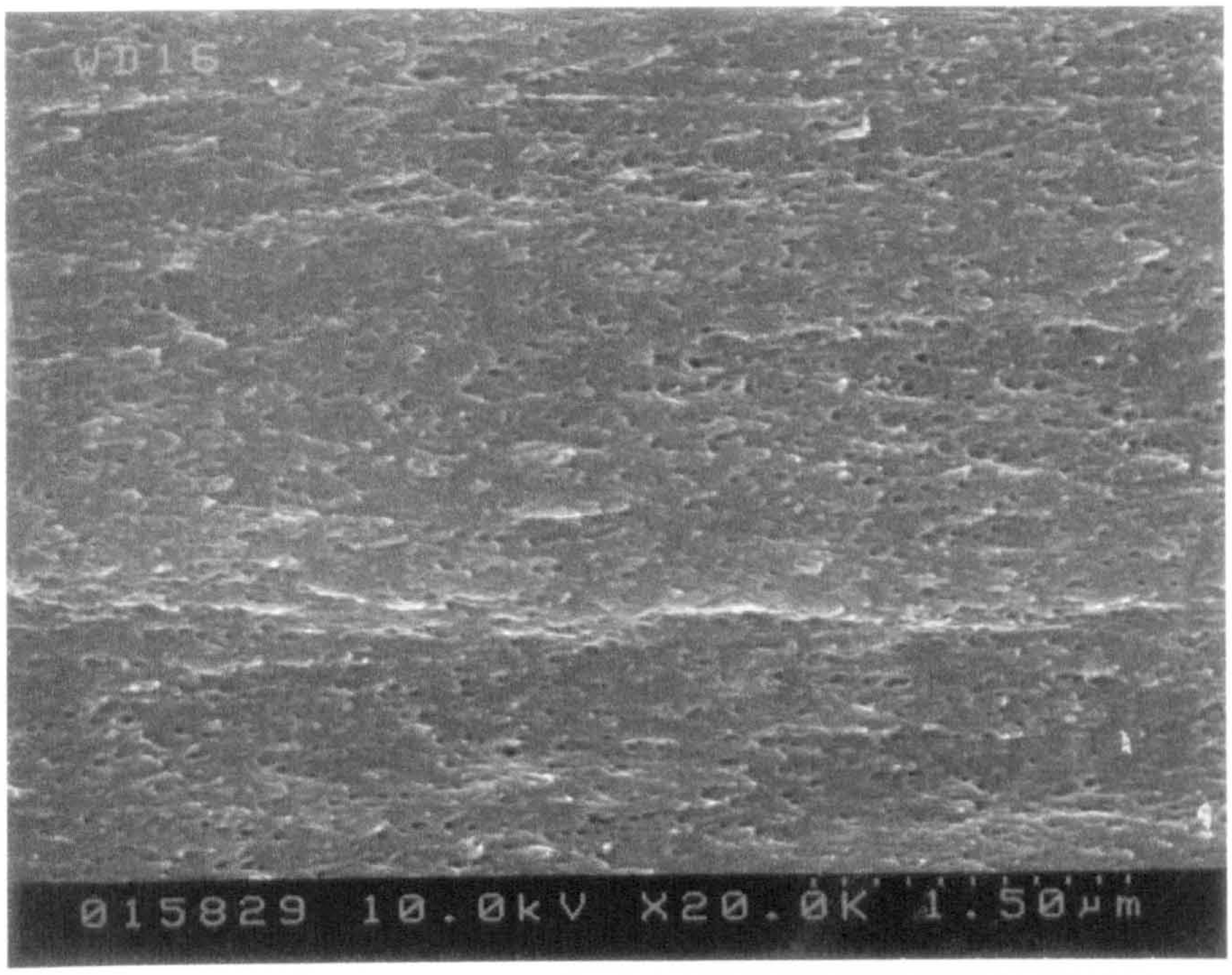

Fig. 3. 9. Emulsion processed at low temperature (20,000X).
Smaller microvoids are visible here.

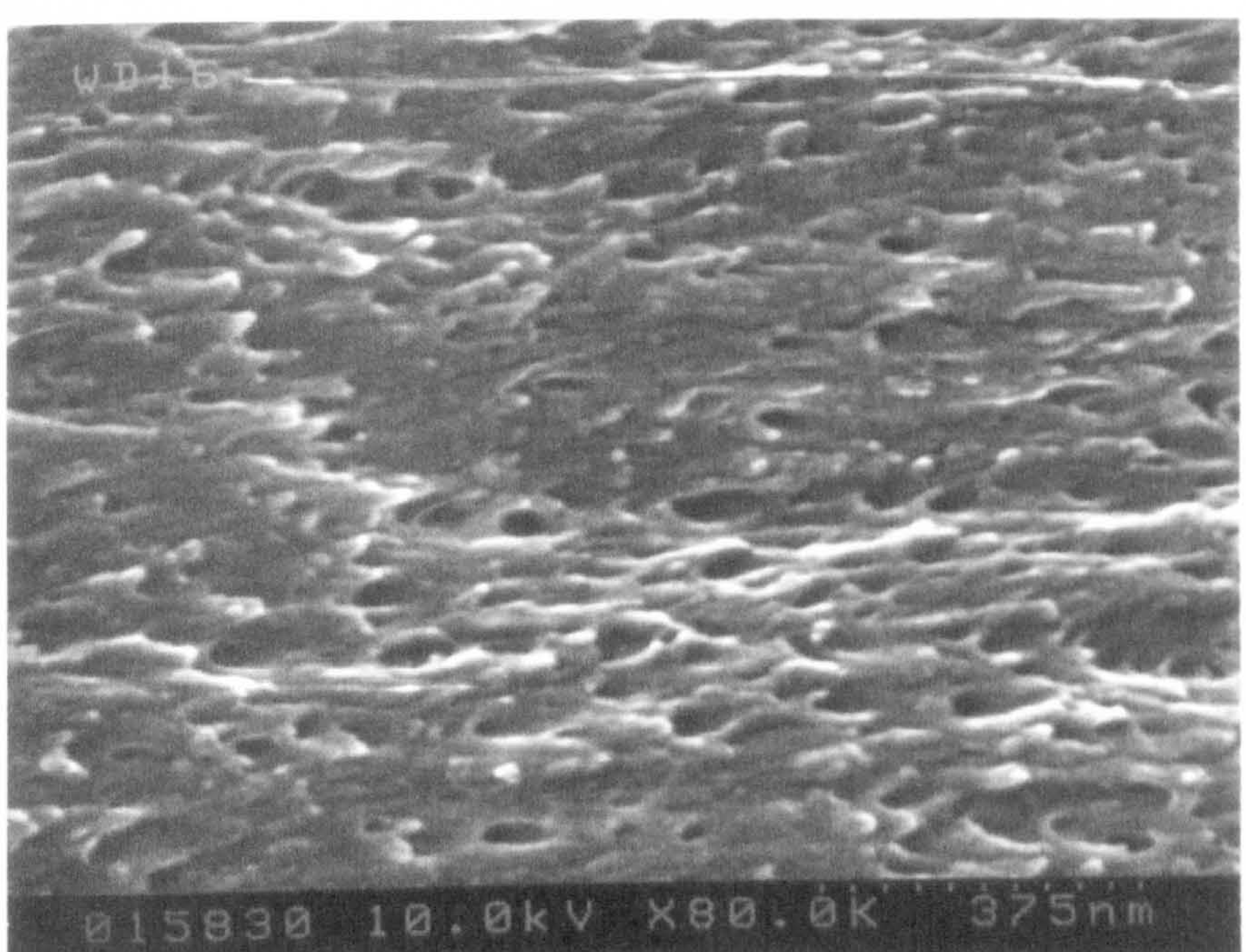

Fig. 3. 10 The same emulsion as in Fig. 3. 8 at a higher magnification (80,000X). Small microvoids (50 nm) are now clearly visible in 1 µm emulsion cross section.

3.8 Conclusions

New SHSG processes for Slavich materials, in particular, for the manufacturing of high quality, high-efficiency HOEs of the reflection type have been introduced. By better understanding the gelatin hardening process and its role in SHSG processing, a process for ultra-fine-grain AgHal emulsions and, in particular, for the Slavich materials: PFG-03M and PFG-03C have been found. The effect of selective hardening has been investigated to find the optimum hardening condition for the SHSG process applied to Slavich materials. By adding a chrome hardener to a modified PBU-metol bleach solution, and, after that, introducing a warm water bath for gelatin cross-linking to occur, followed by additional surface hardening in formaldehyde vapor, slow fixing and isopropanol dehydration, high-efficiency HOEs can be obtained.

The new SHSG processing of Slavich AgHal emulsions is most suitable for reflection HOEs. However, in addition to previous successful technique for transmission HOEs, the new reflection SHSG processing can also be used for transmission HOEs recorded on the ultra-fine-grain AgHal emulsions. The highest quality transmission or reflection HOEs are always obtained employing the ultra-fine-grain AgHal emulsions. The work on SHSG processing will be continued in order to further improve the process and, if possible, to make it simpler and safer, which means, e.g., by finding a replacement for the formaldehyde vapor-hardening step.

Using the new SHSG process, color HOEs as well as monochrome and color display holograms can be produced. Because of the relatively high sensitivity of the Slavich materials compared with DCG and photopolymer materials, large optical elements can be manufactured, only limited by the size of available holographic glass plates.

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Chapter 4

SHSG Processing for Colour HOEs

4.1 Introduction

New techniques for recording and processing silver halide sensitized gelatin (SHSG) holograms recorded in different types of commercial silver halide (AgHal) materials have been described in Chapter 2 and Chapter 3. In addition, there have been several recent papers on the SHSG technique published by other authors. [4.1-5] The advantage of SHSG holograms over the dichromated gelatin (DCG) ones is the high sensitivity of the AgHal emulsion and the possibility to sensitize such materials over the entire visible part of the light spectrum. The most difficult type of holographic optical elements (HOEs) is the reflection type recorded in three wavelengths because much higher spatial frequencies are recorded in colour reflection holograms than in HOEs of the transmission type.

Recently two kind of ultrafine-grain AgHal emulsions have been introduced by Slavich [4.6, 7] and by Holographic Recording Technologies GmbH. [4.8] The BB-type of materials from HRT were originally produced in Germany but now these emulsions are manufactured in England by Colourholographic Ltd. [4.9] Ultrafine-grain emulsions (grain size: 10 - 20 nm) from these companies are suitable for recording SHSG holograms of the reflection type. When such materials are employed, colour reflection HOEs can be manufactured with a better quality than that recorded in DCG materials. Because of the need for finer interference patterns to be recorded in colour reflection HOEs, a new process had to be developed.

To improve the reflection SHSG process for the colour HOEs, intermediate drying process and the bleaching in terms of pH of the bleaching solution and concentration of chromium ion have been investigated more finely.

4.2 Drying of Processed AgHal Emulsion

As discussed in paragraph 2.5, the condition of the drying process is one of the most important variables in holographic processes, which directly influence the characteristics of the AgHal holograms. The factors that can affect the quality of holograms are the drying method including solutions used in the dehydration process, temperature, drying speed and humidity. The drying procedure of holograms has been discussed by Burckhardt and Doherty [4.10] who concluded that the drying method had an influence on the quality of holograms. Hariharan found that the alcohol used at the drying procedure critically affected the quality of holograms. [4.11]

As described in Chapter 2, various solvents have been used in the drying procedure to reduce the run-time of the drying machine and to improve uniformity of HOEs. In the SHSG process for reflective HOEs described in Chapter 3, the intermediate drying procedure just before the vapour hardening step is quite important because the unevenness of emulsion surface may have a negative influence on the HOE characteristics. Unfortunately, two kind of uneven fringes were formed after drying procedure, which is shown in Fig. 4.1 and Fig. 4.2. The first one shown in Fig. 4.1 was caused by the change in environmental conditions of temperature and humidity. It can be avoided by using desiccators with constant temperature and controllable humidity. But, in the case of large HOEs, it is very hard to obtain uniformity and it takes more than an hour for the HOEs to dry. Thus the drying machine, which will be described in paragraph 6.2.1, has been applied to the drying procedure. The second fringe shown in Fig. 4.2 seems to be caused by the usage of pure solvent at the final drying step. When wet emulsion is soaked into a pure solvent, the dehydration takes place so rapidly that there is a difference of dehydration speed between exposed and unexposed zones in the emulsion. This phenomenon causes the fringes shown in Fig. 4. 2.

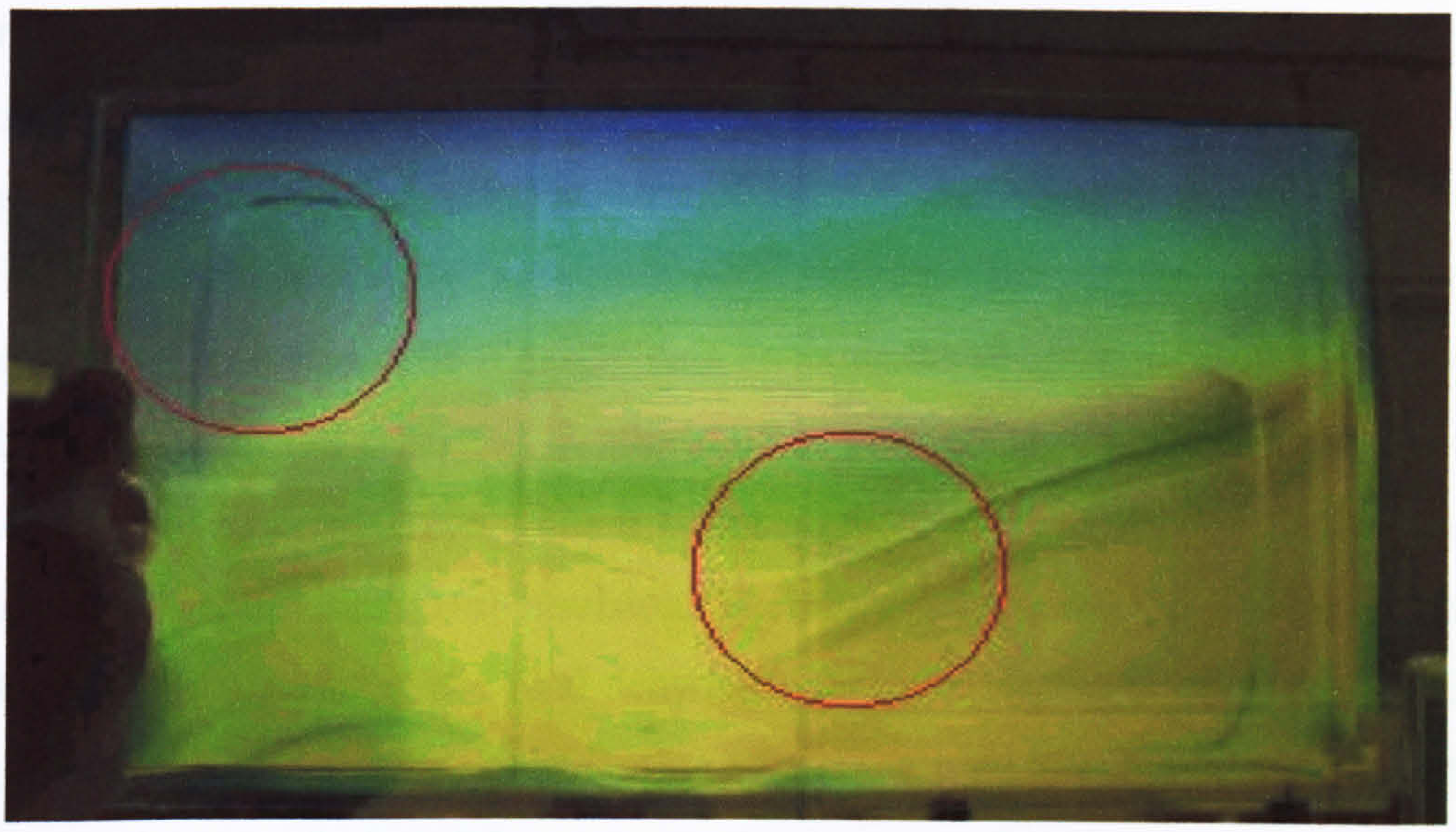

Fig. 4. 1 Uneven fringes caused by change in conditions during drying procedure

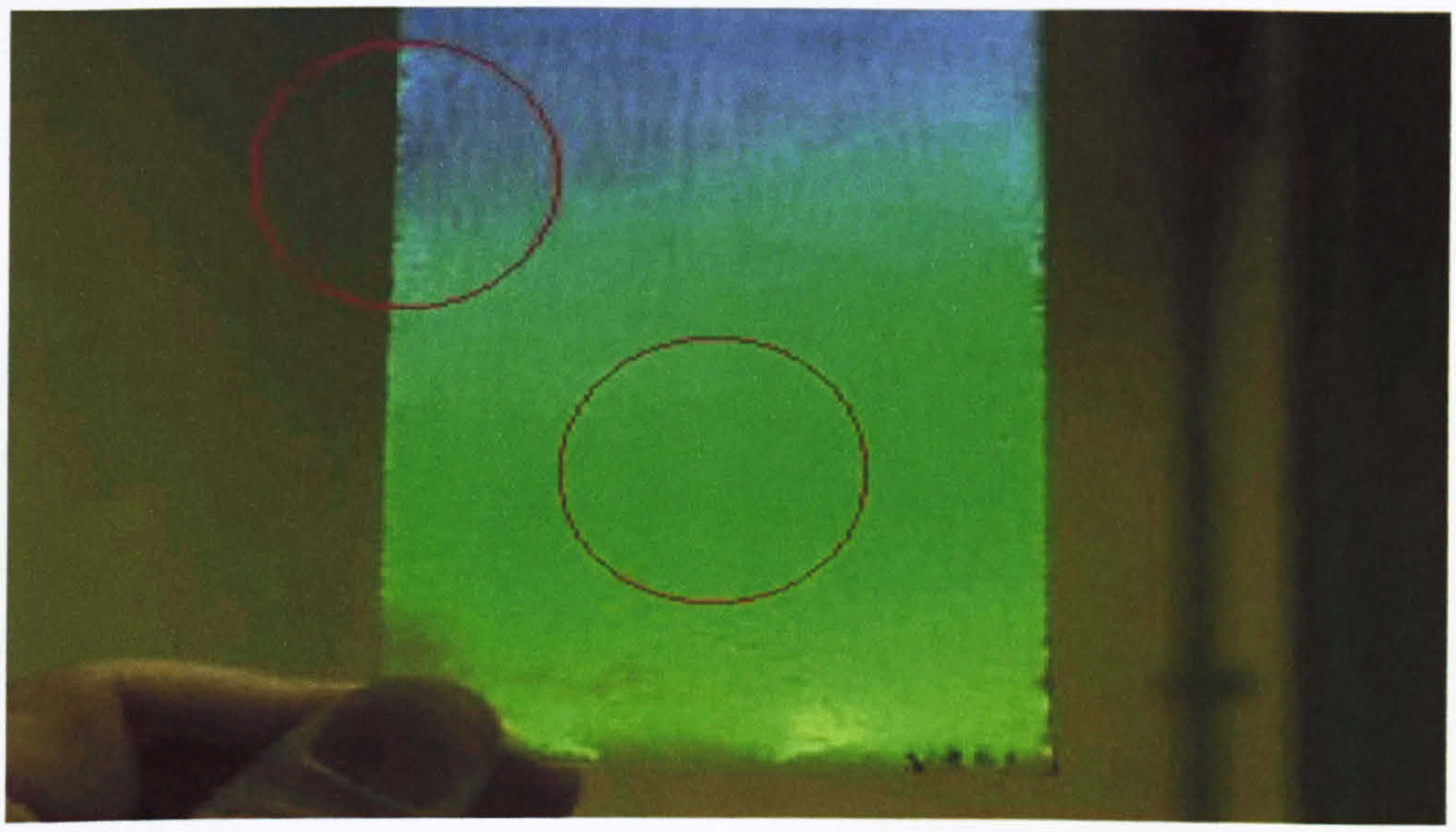

Fig. 4. 2 Uneven fringes caused by the pure solvent in the drying procedure

Several experiments have been carried out to find the optimal condition of the drying procedure using solvents such as ethanol and methanol at the intermediate dehydration step. The surface profiles of the dried emulsion, measured by a surface profile mapping system are illustrated in Fig. 4.3, 4.4 and Fig. 4.5. SPM (scanning probe microscopy) has been used as a surface profile mapping system. SPM has been normally used to measure surface morphology of materials using a non-contact probe. In each figure, the upper part represents the microscopic morphology and the area of scanning is 100μm × 100μm. The lower part shows global roughness of which scanning area is 3mm × 3mm. As can be seen in Fig. 4.3 and Fig. 4.4, both global roughness of samples dried using pure ethanol and methanol were not good enough for HOEs. The microscopic uniformity has no meaning because the data contains the roughness of glass substrate on which AgHal emulsion is coated. It appears that both ethanol and methanol cause that problem explained previously. Thus it is not preferable to use pure (100%) solvent in the drying procedure of AgHal emulsion. Therefore solvent with lower concentration, e.g. 80% should be used at the final dehydration step to avoid this problem. The result using a solvent bath with the concentration of 80% is shown in Fig. 4.5. In addition, a drying chamber may be helpful to get rid of solution at the surface or moisture in the emulsion. A linear nozzle air knife followed by a stream of hot air also has been used to remove surface moisture. The drying chamber will be described at Chapter 6 in detail. Fig 4.5 shows the great improvement of global roughness using 80% ethanol concentration.

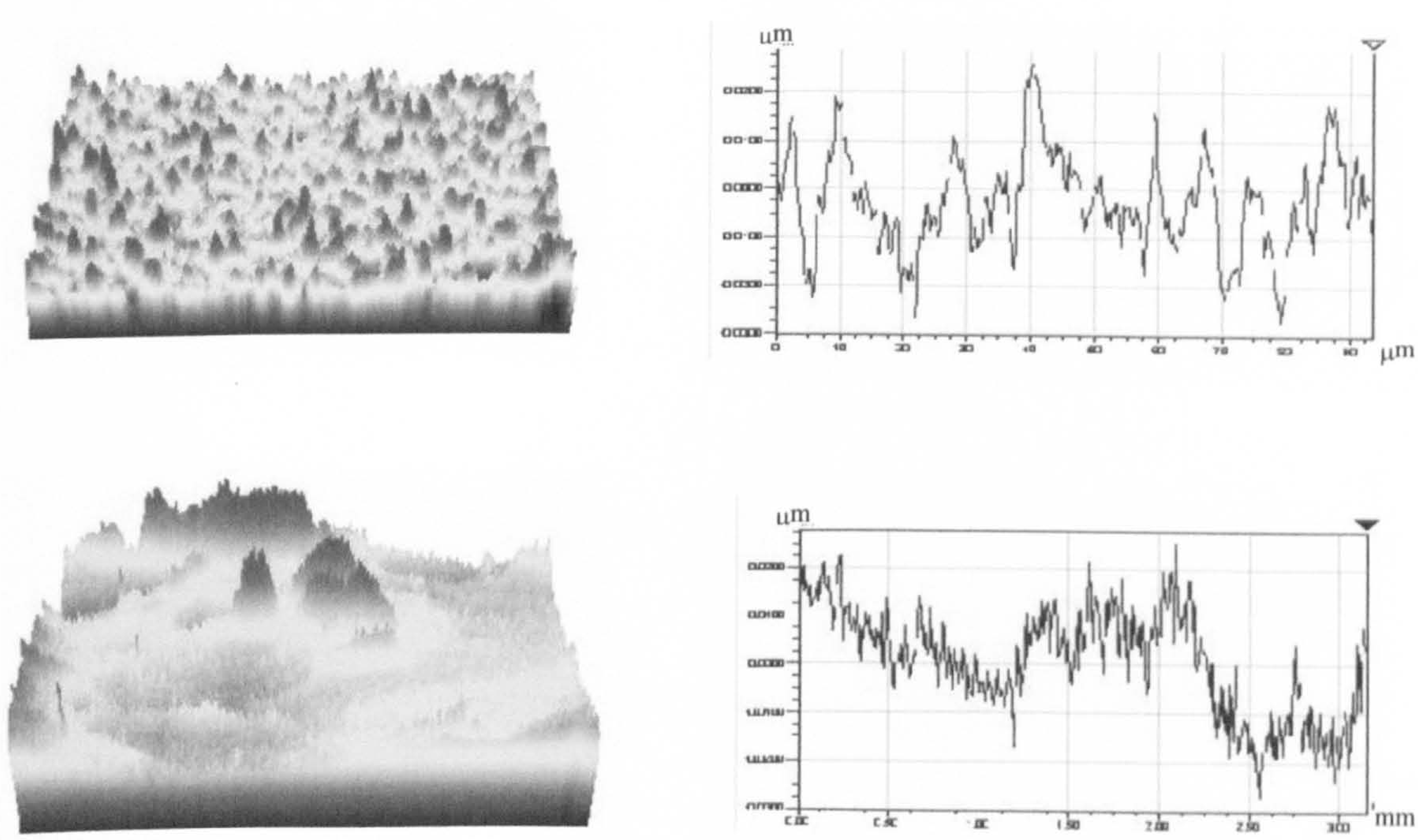

Fig. 4. 3 Surface profile of the emulsion dried in the 100% ethanol

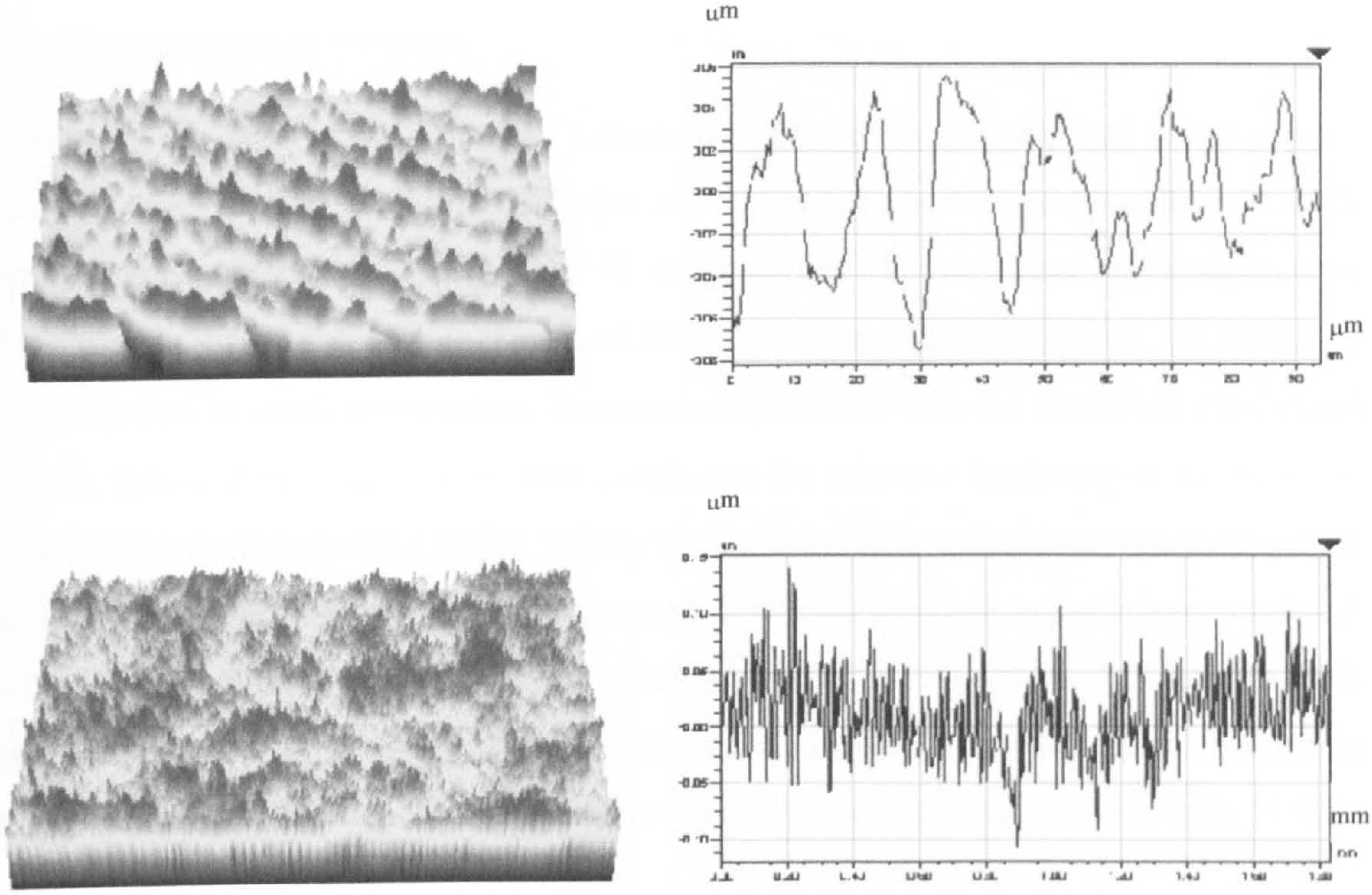

Fig. 4. 4 Surface profile of the emulsion dried in the 100% methanol

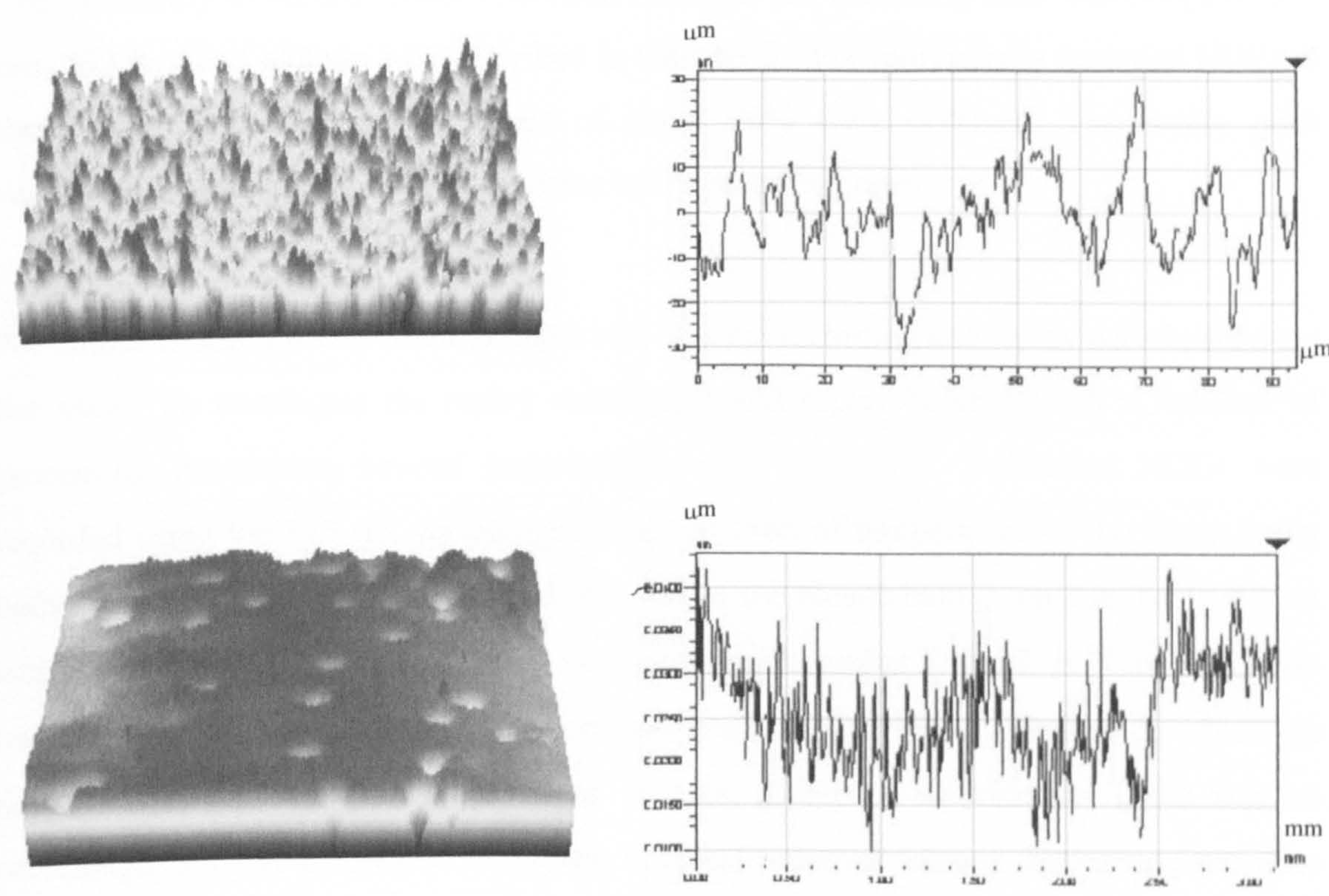

Fig. 4. 5 Surface profile of the emulsion dried in the 80% methanol

4.3 Optimized SHSG Processing for Colour Reflection HOEs and Experimental Results

Previously the process for recording reflection HOEs has been optimized using a single laser wavelength. This time three different recordings have been superimposed in a single emulsion layer. Red (647 nm), green (532 nm) and blue (458 nm) laser wavelengths have been used to record colour holograms and HOEs. As described in Chapter 3, the bleaching is performed at room temperature (approximately 22°C) with the modified PBU-metol bleach, followed by a warm water bath to enhance the selective hardening of the emulsion to avoid large rehalogenated grains. To dry the emulsion before the vapour-hardening step, an industrial methylated spirit was used instead of ethanol to obtain better colour control. A 50% glutaraldehyde [CH_2 $(CH_2CHO)_2$] solution replaced previously used formaldehyde to generate vapour for the dry emulsion hardening step to minimize the vapour hardening time. Glutaraldehyde reacts some 3600 times faster than formaldehyde with gelatin. [4.12]

The possibility to record colour reflection HOEs at the following laser wavelengths: 647 nm, 532 nm, and 458 nm was described in Chapter 3. For individually recorded HOEs at these three wavelengths, DE values of about 96% were obtained. The replay peak wavelengths were almost exactly the same as the recording ones.

For colour HOEs it is important to make sure that the recording and replay wavelengths are the same. To investigate the replay wavelength and replay bandwidth as a function of processing parameters, several experiments were performed. Reflection HOEs were recorded using the 515 nm wavelength. The variation of temperature of the warm water bath (Step 4 in Table 3.2) was studied. The pH of the bleach bath (Step 3 in Table 3.2) as well as the treatment time in the vapour-hardening chamber (Step 7 in Table 3.2) was investigated. The experimental conditions are found in Table 4.1. The results, which are illustrated in Fig. 4.6, indicate a slight increase in replay wavelength. There was no wavelength shift as a function of bleach bath pH value or vapour hardening time. The bandwidth, however, is decreased when the pH value of the bleach increases. It is also decreased when vapour-hardening time is increased. It seems that both factors are related to the definition of boundaries of fringes or confinement of fringes. When the pH of the bleach approaches a value of 6, the bleaching speed starts to decrease and stain appears in the emulsion after processing.

Table 4.1. SHSG processing experiments

Sample	pH	Vapour Hardening (min)	Replay Wavelength (nm)	Replay Bandwidth (nm)
1	4	10	517	44
2	4	25	516	39
3	4	40	518	30
4	5	10	516	36
5	5	25	517	29
6	5	40	518	28
7	6	10	517	31
8	6	25	519	25
9	6	40	517	20

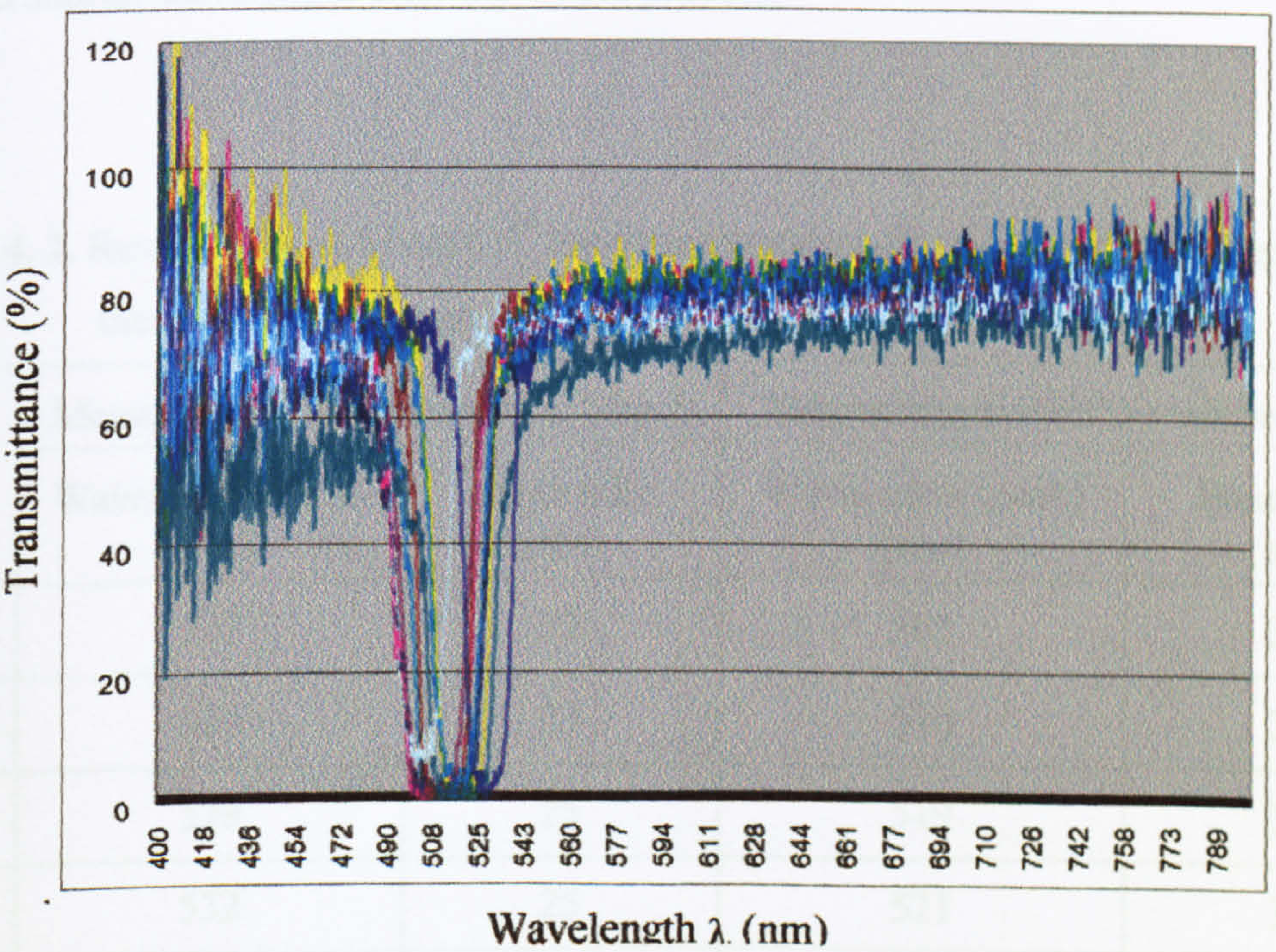

Fig. 4. 6 Measurements of pH concentration (bleach) and vapour hardening time tests.

Another performed experiment was a study of Cr^{2+} ion concentration of the bleach bath. Here HOE transmittance was measured in the middle of the process, after the drying step but before vapour hardening (Step 5 in Table 3.2). Then, after the final processing step, transmittance measurements were repeated. The results are shown in Table 4.2 and Fig. 4. 7 and 4. 8. These results indicate that a Cr^{2+} ion concentration between 1 and 2 % is necessary in the bleach bath to obtain HOEs which replay at the recording wavelength. Table 4.2 and Fig. 4.7 show that the wavelength was shifted toward longer wavelength than recording wavelength after processing step 5. With increased Cr^{2+} ion concentration the HOE-replay is shifted towards longer wavelengths. The high acidity greatly influenced on the swelling of gelatin and AgHal emulsion.

As explained previously, the gelatin structure easily shrunk or collapsed to some degree in the fixing and the dehydration step, where all AgHal grains were dissolved away and pure gelatin structure with microvoids was formed. Thus it is necessary to swell the emulsion before fixing step to control the thickness (or the degree of swelling). As a result of this treatment, the wavelength returned to the recording wavelength or moved toward shorter wavelength after the whole process.

Table 4. 2. Results of bleach bath Cr^{2+} ion concentration tests, measured after Step 5,and at the end of the process.

Cr^{2+} (%)	Measurements after processing Step 5		Measurements after the whole process	
	Wavelength (peak) (nm)	Bandwidth (nm)	Wavelength (peak) (nm)	Bandwidth (nm)
0.1	522	22	501	34
1	526	25	510	38
2	529	25	519	39
3	532	25	521	32
5	542	22	524	32
10	551	22	531	34

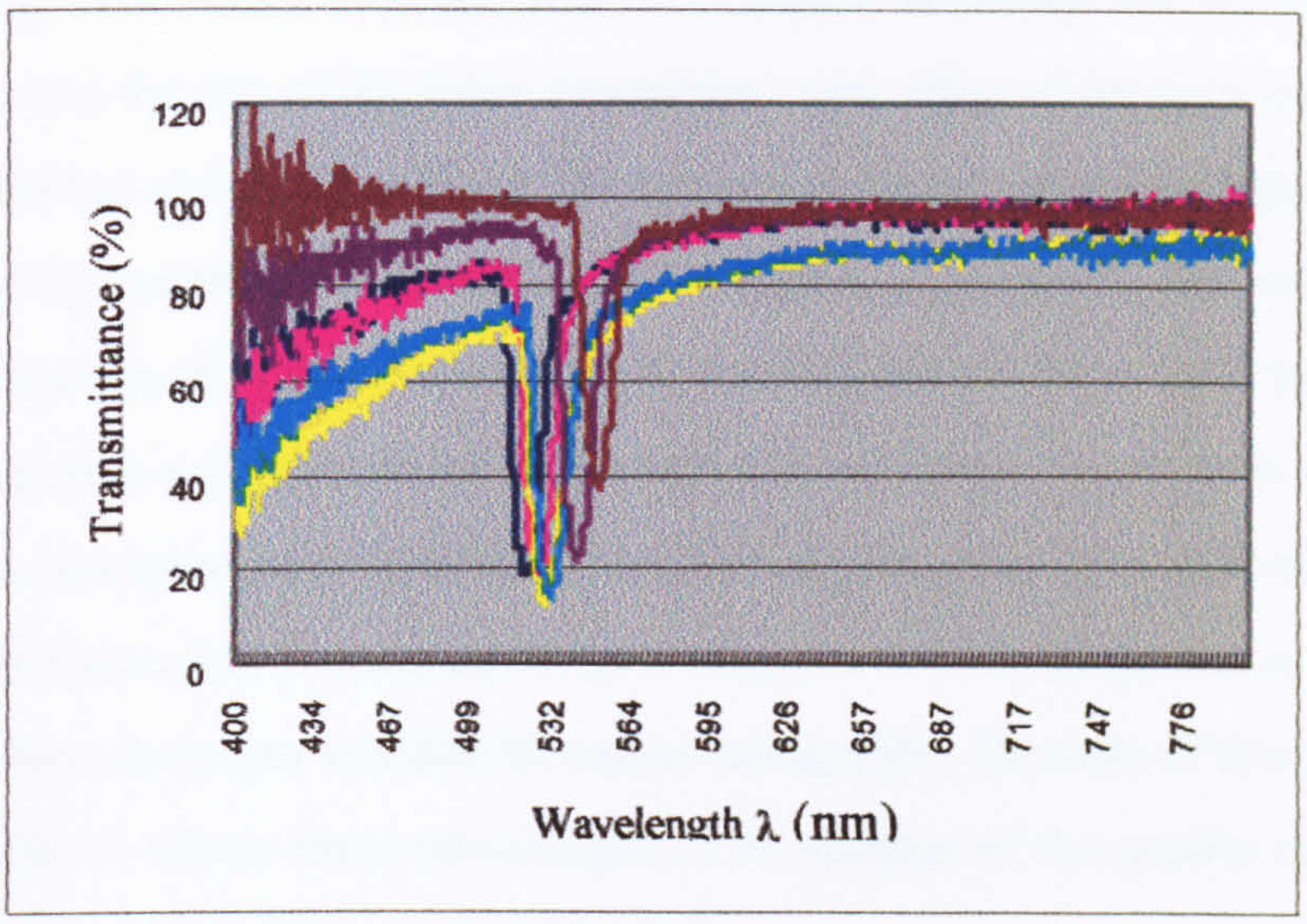

Fig. 4. 7 Bleach bath Cr^{2+} ion concentration tests (measurements after Step 5 of the process)

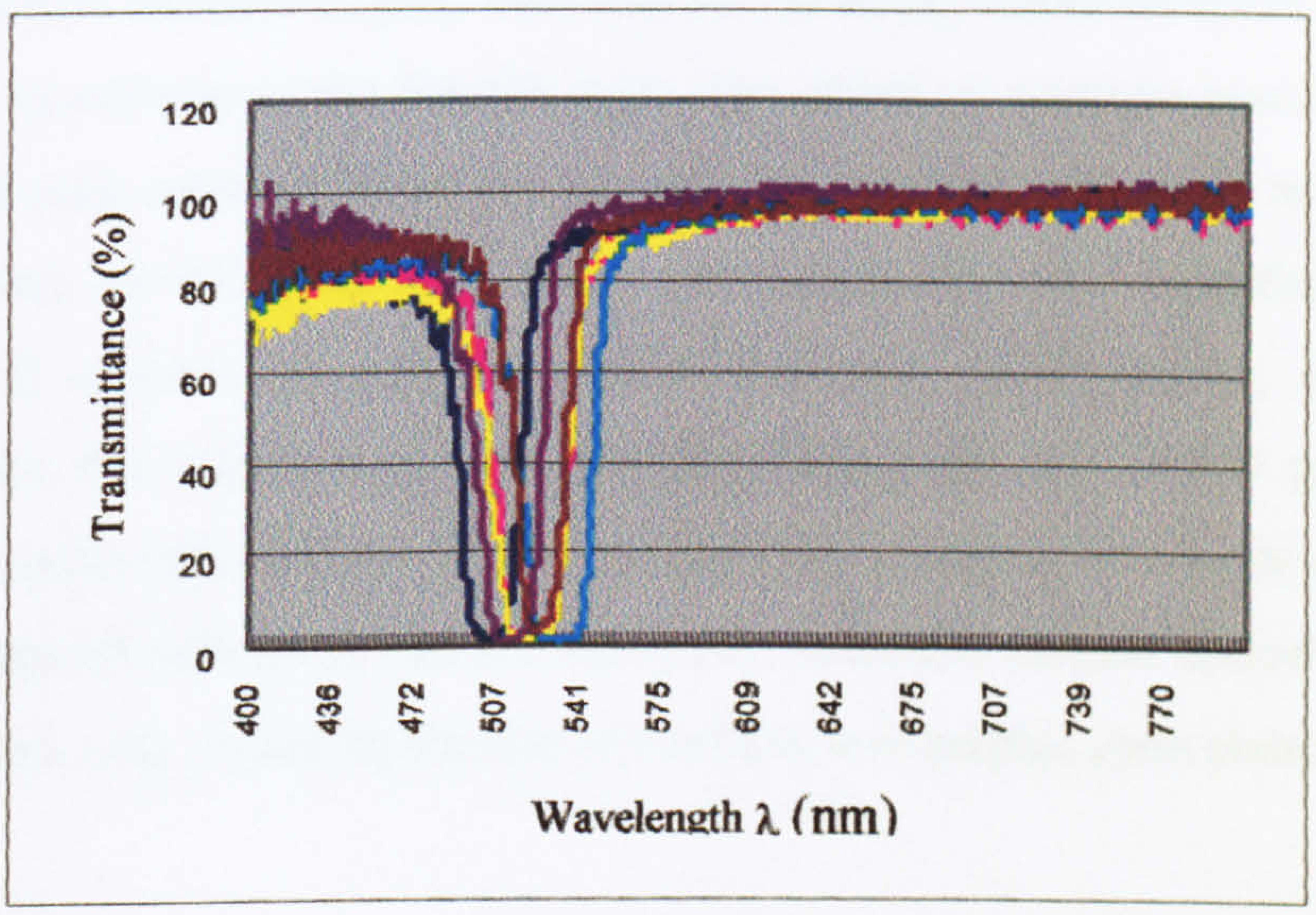

Fig. 4. 8 Bleach bath Cr^{2+} ion concentration tests (measurements after the finished process)

Results of multiple exposed HOEs were rather good with the replay wavelengths identical to the recording ones, which indicates that no emulsion shrinkage has occurred. However, overall quality and the DE of the three recordings were affected by poor quality of recent PFG-03C emulsion batches. In addition, the red and green sensitivities of the panchromatic emulsion were very uneven. The emulsion had a high red sensitivity, four times larger than green. An indication that the emulsion was not optimized for colour holography was revealed by a greenish appearance of the unexposed emulsion. To perform well for colour holography, the unexposed emulsion has to be more or less clear or at least only show a hint of gray stain. It seems that Slavich has tried to improve red sensitivity but at the same time made the emulsion no longer suitable for colour holography. Because of this problem, it has not been possible to obtain three-wavelength HOE samples of the quality expected until a suitable panchromatic emulsion can be obtained.

4.4 Conclusion

The SHSG process has been slightly modified for recording colour HOEs in ultrafine-grain panchromatic emulsions of the Slavich type. The effect of multiple recording has been investigated in such emulsion to be able to make three-colour holograms and three-colour HOEs. The work on the SHSG processing will continue in order to further improve the process and, if possible, to make it simpler and safer, which means, e.g., finding a replacement for the vapour hardening step. Employing the new SHSG process, colour HOEs can be produced. Because of the relative high energetic sensitivity of the Slavich materials compared with DCG and photopolymer materials, various optical elements can be manufactured, only limited by the size of available holographic glass plates.

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Chapter 5

Replication of Diffusers Using SHSG Processing

5. 1 Diffusers for Display Devices

Nowadays the display market has been increasing rapidly caused by the growth of multimedia applications. The dominating device in the display market is the LCD (liquid crystal display), which is the non-emissive flat panel display. LCDs are used in direct-viewing monitors or TVs, compact displays for PDAs (personal data assistants) such as palm-top or laptop computers, hand-held phones, etc. There are some requirements for the mobile application of LCDs. First of all, low power consumption is essential since batteries for mobile applications currently take up a large portion of the devices' size and weight. Next one is brightness. Brightness is quite essential because the displays should be bright enough to be viewable in daylight. Other demands are: contrast ratio, uniformity and colour or grayscale representing capability.

The brightness is critical for LCDs because they are non-emissive and should have a very compact structure similar to an edge-lit illuminator, which will be described in paragraph 5.3. These factors are regarded as barriers against the improvement of brightness of LCDs. The best ways to obtain high light efficiency are to change the structure of the LCD itself, i.e., to enlarge the opening ratio of each pixel, to substitute the polarizer with another optical element, which provides polarized light to the LCD panel, and to put more lamps alongside the edge of panel. But the structural change costs a great deal and there is a limitation because of the requirements for the shape of devices containing LCDs. Preferably, the shape of LCDs should be compact, thin and lightweight.

A possible way to achieve high light efficiency is to substitute the numbers of optical elements in the illuminating device with a single element with higher quality. Fig. 5.1 is a schematic diagram of a typical back-illuminator for transmission type LCD, which is called backlight. LCD backlights consist of many components like a CCFL (cold cathode fluorescent lamp), a waveguding wedge prism, a reflector, a few optical elements and several diffusers. The functions of each optical element will be discussed later in detail.

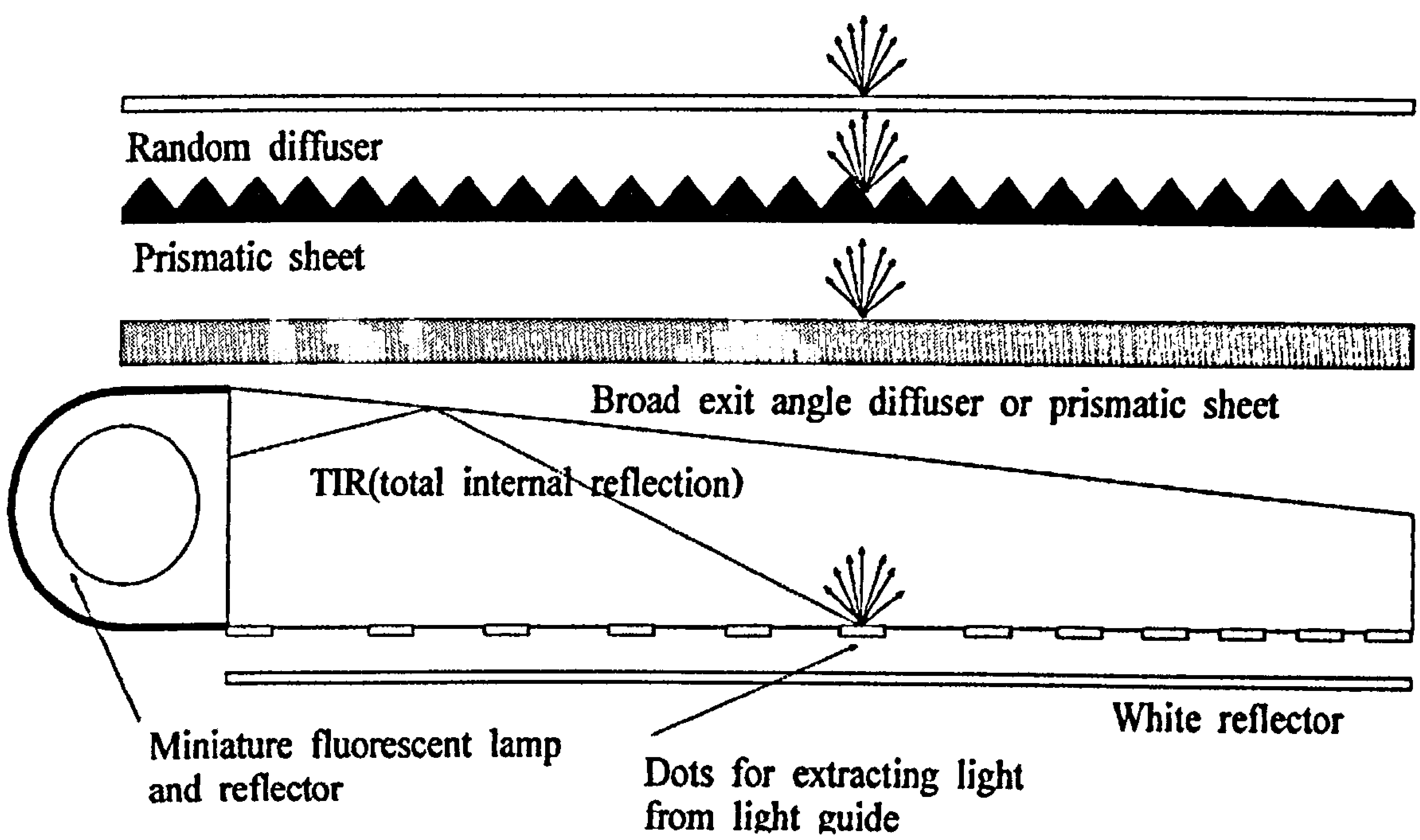


Fig. 5. 1 Typical back-illuminator for transmission type LCD

Diffusers play an especially important role in LCD application as a beam shaping device, brightness homogenizer, light scattering device and as an imaging screen. The specific features required for individual applications are not all the same, but the transmittance and diffusing angle are common characteristics in all applications. In any LCD application such as direct viewing (transmissive and reflective) LCDs and projection LCDs, the brightness and viewing angle can be improved by using HOEs such as holographic reflectors, holographic colour filters and holographic diffusers. In this section, a method of copying diffusers using the SHSG process will be described, which improves the characteristics of diffusers.

5. 2 Replication of Diffusers

5.2.1 Selection of Source Diffuser for the Replication

Ground glass, white plastic, opal glass, polycarbonate and polyethylene diffusers, common in the marketplace, could be copied onto recording materials using a holographic method. First of all, in order to find the diffuser, which is suitable for the replication, i.e. diffusers with stronger transmittance and wider diffusing angle, various diffusers have been examined. The measurements of transmitted light intensity were performed using the optical setup shown in Fig. 5.2, where the photo detector head moved on the optical rail along the screen surface. The diffusing angles were calculated from the equation,

$$\theta = \tan^{-1}(x/L) \tag{5.1}$$

where x is the distance from the center of screen to the position of detector and L is the spacing between diffuser and screen.

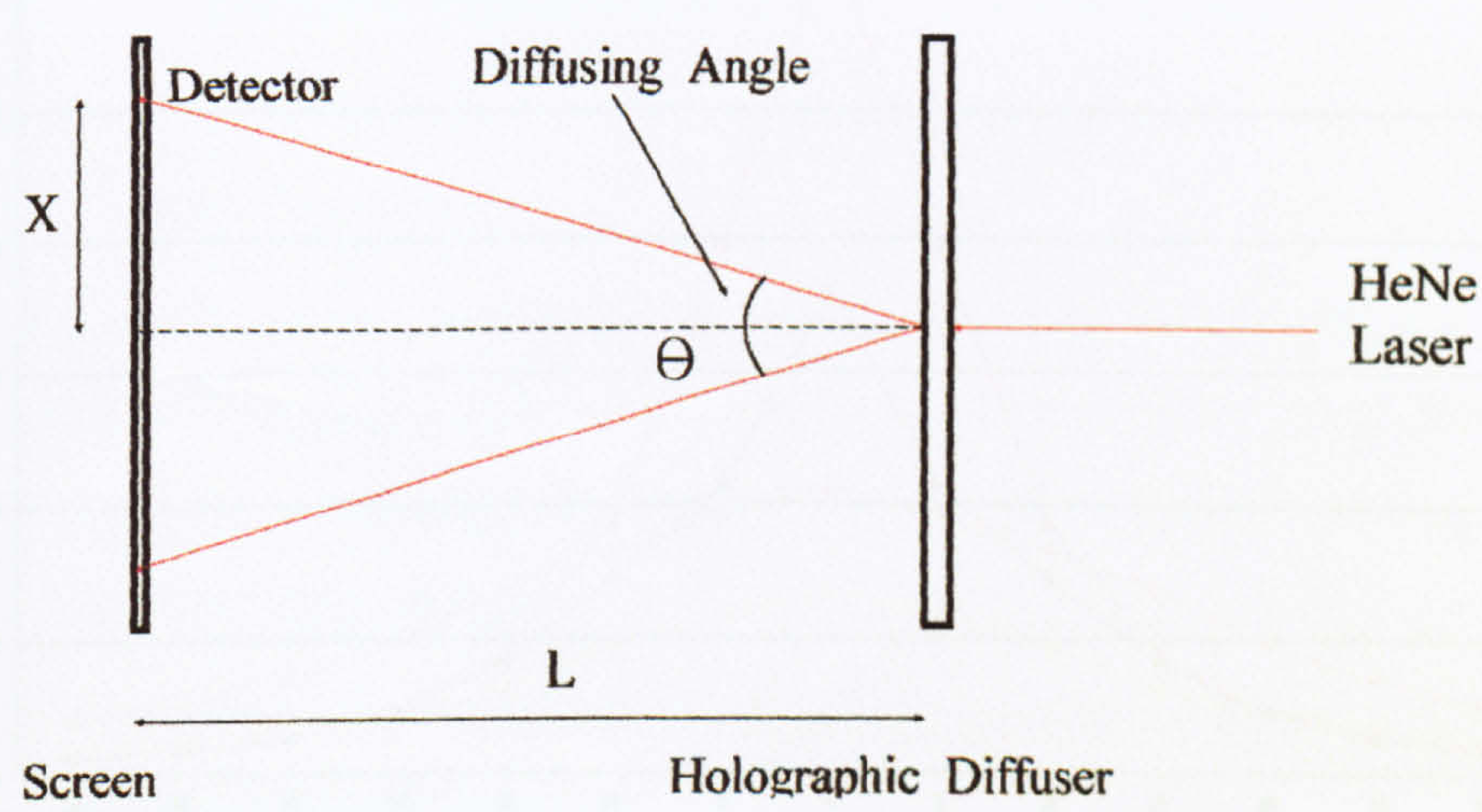


Fig. 5. 2 Optical set-up to measure diffusing angle

The diffusers used in this investigation were as follows:

- Ground glass diffusers polished with coarse polishing powder (#400), the numbers written after glass diffuser mean the number of glass diffusers attached together to improve the diffusivity
- Ground glass diffuser polished with finer polishing powder (#600)
- Polycarbonate diffuser copied using a stamping method onto polycarbonate film
- Normal opal glass diffuser.

The results of the measurement are shown in Fig. 5.3. The opal glass was the best in terms of diffusing angle and uniformity, but the transmittance of that diffuser was lower than other diffusers. Thus opal glass seemed to be a good homogenizer but it could not be used for normal optical system. For the glass diffusers, as the number of diffusers attached together increased, the diffusing angle became wider and but transmittance decreased. If the glass diffuser was finely polished, the diffusing angle got wider than that coarsely polished. The overall qualities of a finely polished glass diffuser and a polycarbonate diffuser are good for the application to diffuser replication.

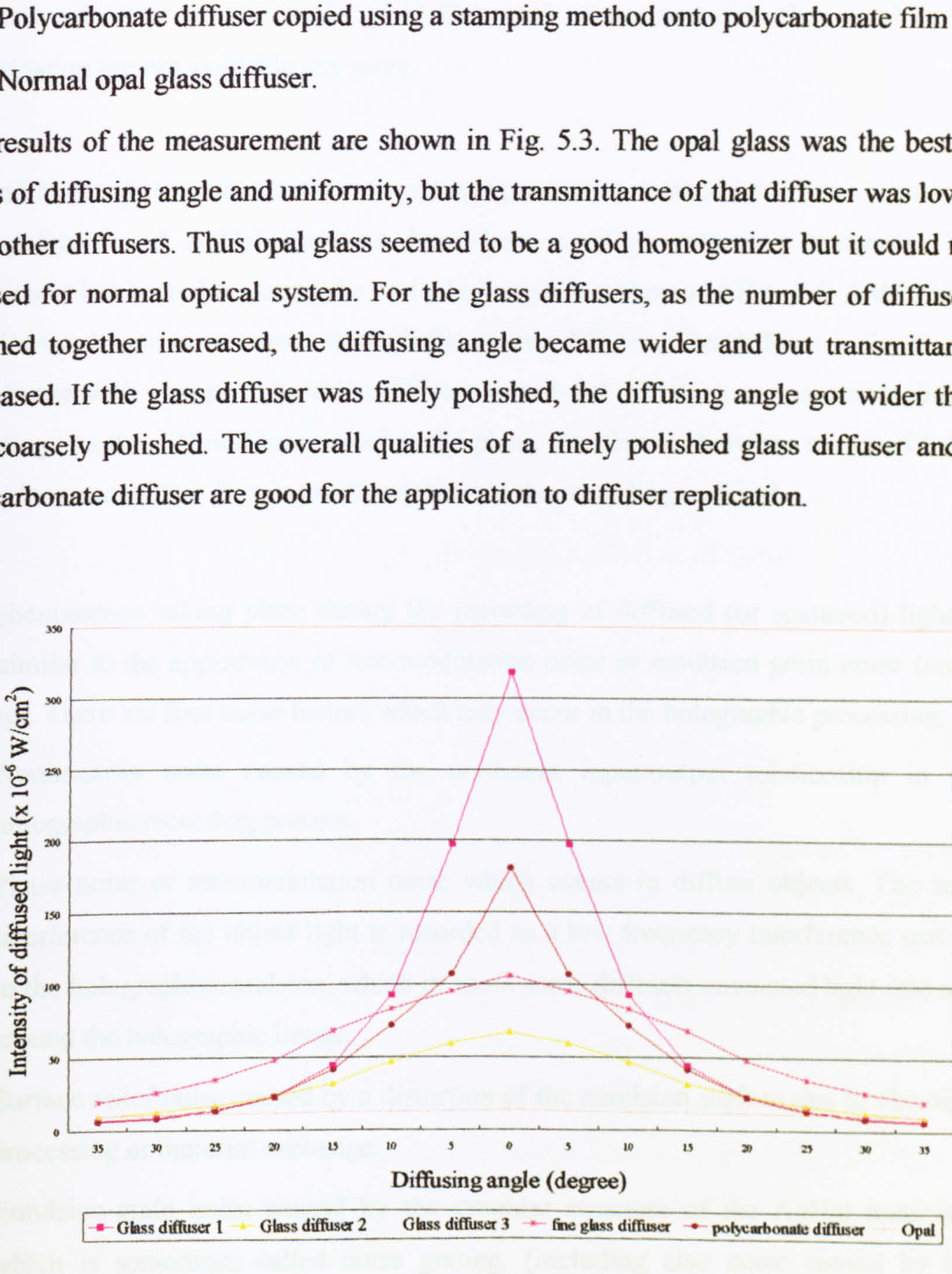


Fig. 5. 3 Diffusing characteristics of various diffusers

5.2.2 Materials and Processes for the Replication

Wadle and his colleagues examined the manufacturing of holographic diffusers using AgHal emulsions (Agfa 8E75 and Kodak 649F) and photopolymers (Polaroid DMP 128, Dupont 600, 705 and 150 series). They concluded that the diffuser copied on photopolymer exhibited strong diffusion over wide angle. But the AgHal diffuser is efficient only over narrow angle. [5.1] But most of the materials they used in the investigation are not available any more.

Several materials available at the moment and processing method have been examined. Photopolymer and AgHal emulsion have been used as recording materials. The experiment has been done using the optical arrangement shown in Fig. 5.4. A diverging or collimated laser bean passes through the source diffuser. The diffuser is fixed on a rigid frame with clamps to hold the diffuser to prevent vibration or movement during recording. As the diffused beam reaches the plate, interference between scattered lights takes place and certain fringes are formed inside the recording material.

The phenomenon taking place during the recording of diffused (or scattered) light is very similar to the appearance of intermodulation noise or emulsion grain noise (noise grating). There are four noise factors which may occur in the holographic processing:

- Nonlinearity noise caused by the nonlinear input-output relationship in the holographic recording process.
- Phase noise or intermodulation noise which occurs in diffuse objects. The self-interference of the object light is recorded as a low frequency interference pattern in the holographic emulsion, which in some cases diffracts unwanted light into and around the holographic image.
- Surface relief noise caused by a distortion of the emulsion surface due to chemical processing or material exchange.
- Emulsion-grain noise caused by the granular structure of the AgHal materials, which is sometimes called noise grating. (including also noise caused by the substrate material on which the emulsion is coated)

Among these noise factors, intermodulation noise and noise grating are the dominant sources of noise in the image of diffuse-object holograms. The formation-mechanism of these two noise factors is almost same as the replication of diffusers using holographic method.

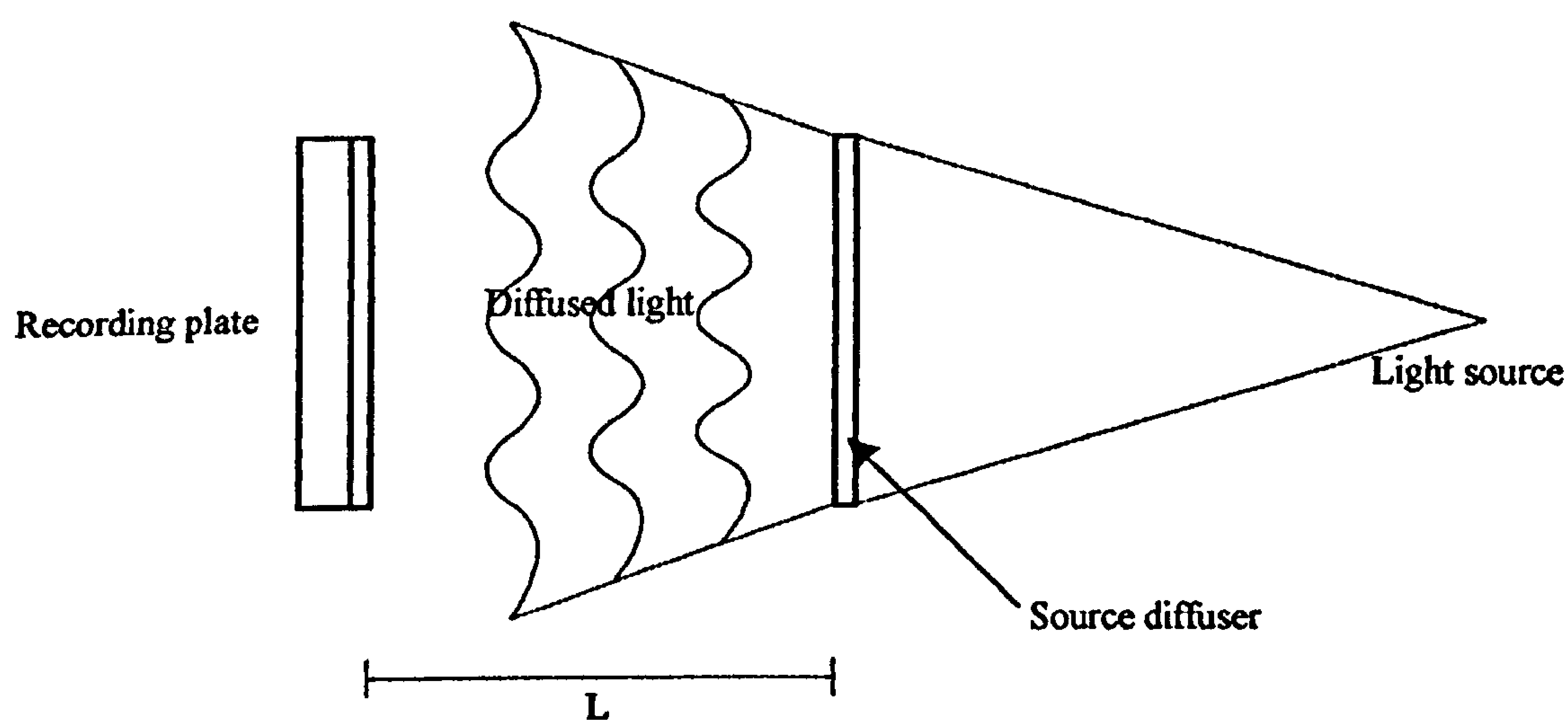


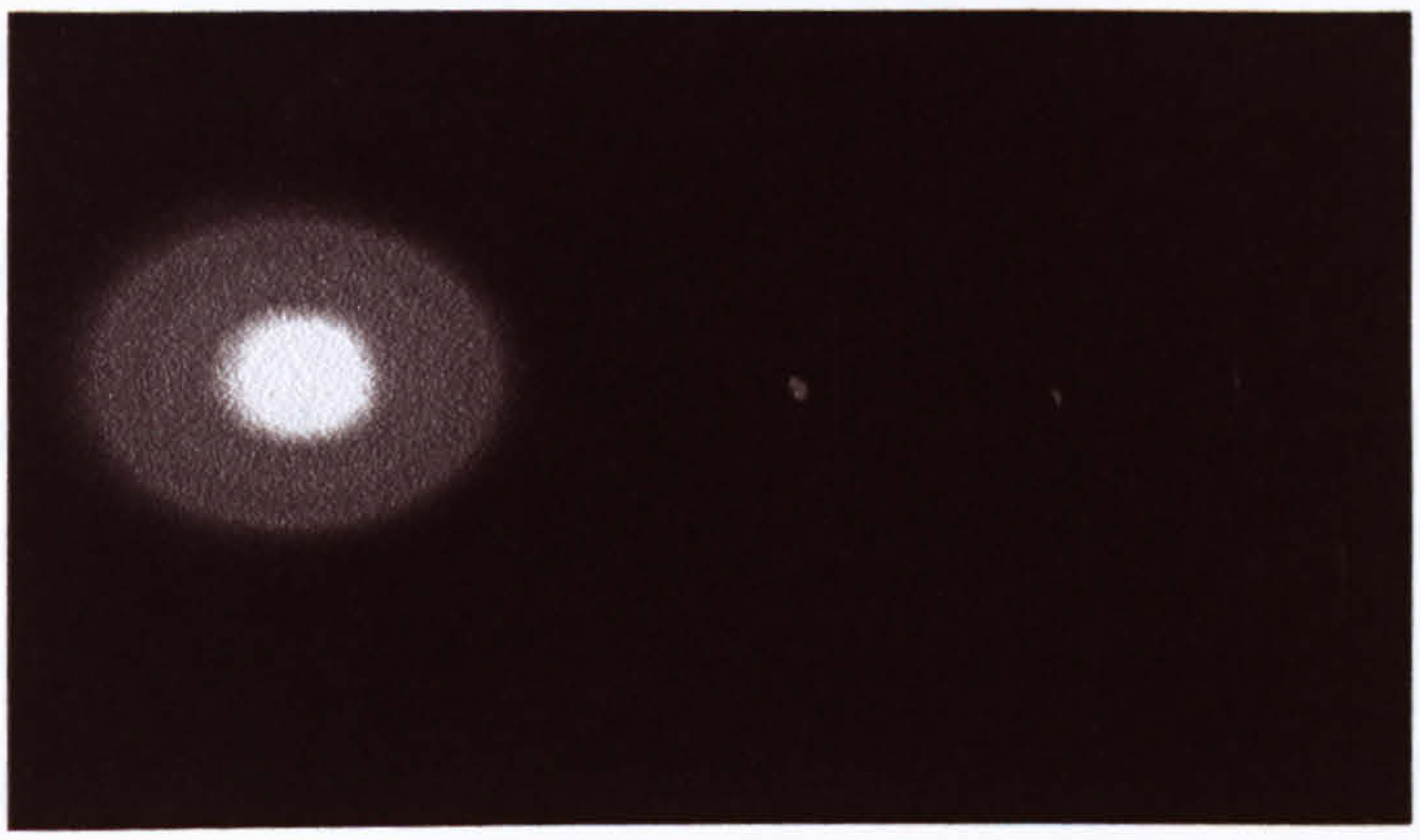
Fig. 5. 4 Optical arrangement for the replication of diffusers

The distance L, which varies from several millimeters to several tens of centimeters, is the spacing between source diffuser and recording plate, determined by the diffusing angle of the source diffuser. Contact copying is not recommended because uneven fringes may occur due to the reflection between the diffuser and the recording plate. Otherwise an index matching liquid should be applied between them during recording. Thus both proximity and projection type of replication leads to better results. Test samples are prepared with POC-80 LS (light shaping) diffuser [5.2] as a source diffuser copied on photopolymers and AgHal emulsions. POC-80 LS (light shaping) diffuser has been produced by an American company, Physical Optics Cooperation [5.3], with transmittance from 85% to 92% according to the wavelength with vertical and horizontal diffusing angles around 80°.

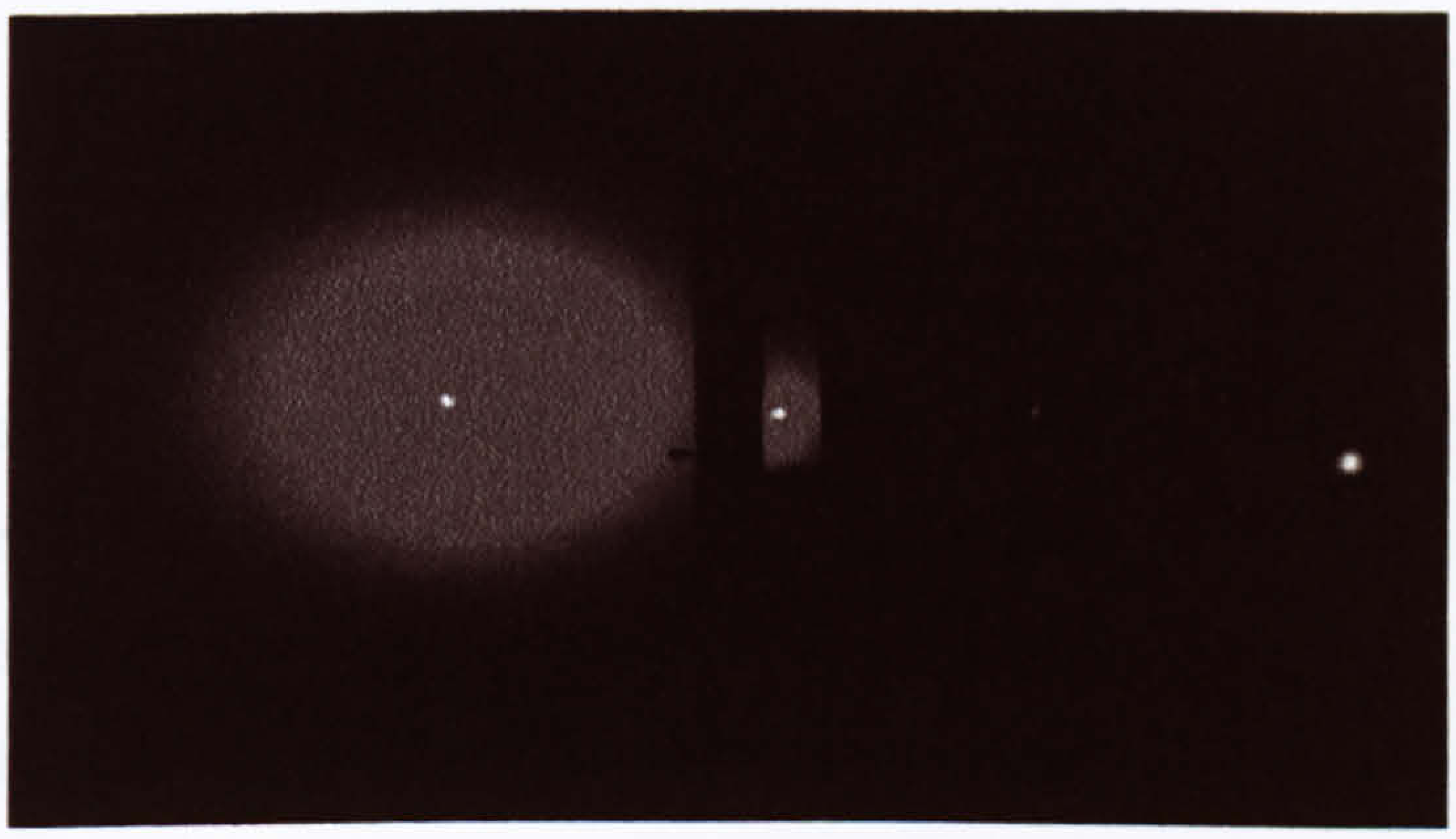
The process used for photopolymers is curing by UV exposure and heat treatment after recording. AgHal emulsions are treated using normal silver halide processing method employing PBU-metol bleach [5.4] or by the SHSG process for transmission HOEs described in Chapter 2. Both the transmission and reflection SHSG processes described in Chapter 2 and Chapter 3 can be used for coping diffusers. In this investigation, the transmission SHSG process has been used since the whole processing time is shorter than the reflection SHSG process. We can use any type of AgHal recording materials such as Millimask (Agfa), VRP and PFG03 (Slavich), and BB plate (Birenheide) for the replication. The Millimask plates were preferred since the emulsion characteristics are consistent from plate-to-plate and the coating quality (uniformity) is better than that of the other emulsions.

In order to quickly get an idea of how good a diffuser is, a brief evaluation has been done, although more quantitative results will be presented in the next section. A point HeNe laser source illuminated the copied diffusers recorded and obtained by different recording and processing methods as mentioned in previous section.

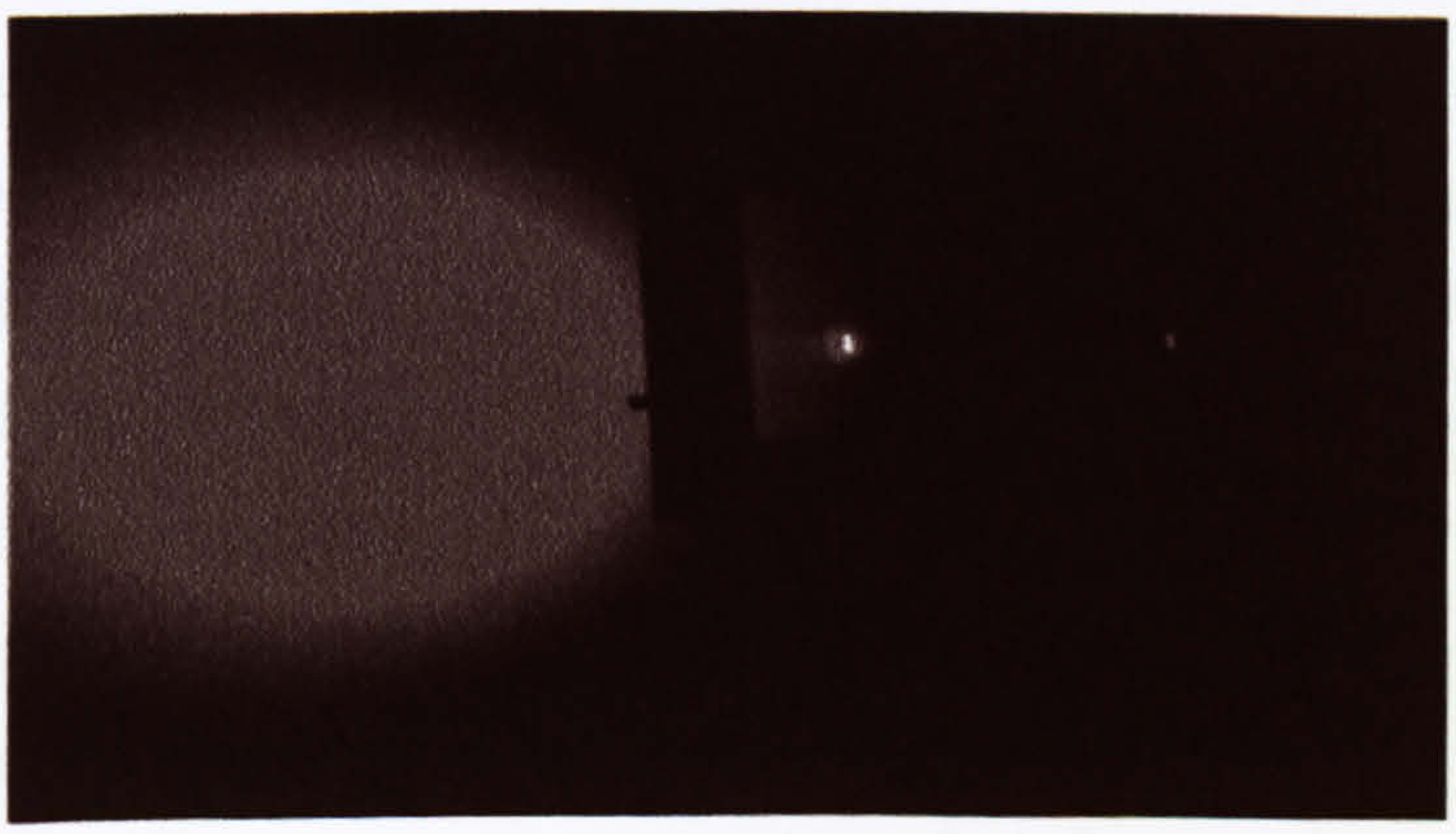
The pictures of diffused light projected on the screen were taken using a digital camera. The results are shown in Fig. 5.5. It was found that the diffusivity of the diffuser copied on photopolymer is not good enough for practical use and there is some transmitted light without diffusion. Diffusers processed with the normal silver halide method seem quite good, but also in this case undiffused light is present. Undiffused light causes glaring and a narrow diffusing angle. According to these results, diffusers copied on SHSG-processed plates represent the best quality.



(a) photopolymer



(b) AgHal emulsion.



(c) SHSG emulsion

Fig. 5. 5 Diffusing characteristic of copied diffuser on various materials

5. 3 Characteristics of Copied Diffusers

5.3.1 Comparison of the AgHal and SHSG Process

As mentioned previously, the diffusing characteristics of diffusers copied on AgHal emulsions seem to be better than those copied on photopolymers. Diffusers processed using SHSG processing have better quality than those processed using normal silver halide processing. Another investigation has been performed to verify the proper process for copying diffusers and to select the adequate source diffuser to replicate. Samples are prepared using various source diffusers and two kinds of processes: normal silver halide process and the SHSG process.

The copied diffuser was illuminated with a point source generated from a HeNe laser and the diffused or scattered light was projected onto a screen. Intensity distribution at FWHM (full width at half maximum) from center toward edge of the projected image has been measured and evaluated. The evaluation of diffusivity was done in the same way as described in the previous section and shown in Fig. 5.2. L has been fixed to 30 cm as a matter of convenience. The typical results are shown Table 5.1 and Fig. 5.6.

Comparing two kinds of diffusers, POC diffusers and ground glass, the POC diffusers have very uniform diffusivity but the transmittance is relatively weaker than that of ground glass. According to this comparison, it seems that there is a trade off between transmittance and diffusing angle. In accordance with the results shown in Table 5.1, Fig. 5.6, the diffusing angle of copied diffusers decrease as transmittance increase. On the contrary, if the transmittance is too high, a hot spot or glaring occurs. The hot spot or glaring affects image quality badly when those diffusers are used in display systems. Thus a compromise value depending on the application should be considered in production of diffusers.

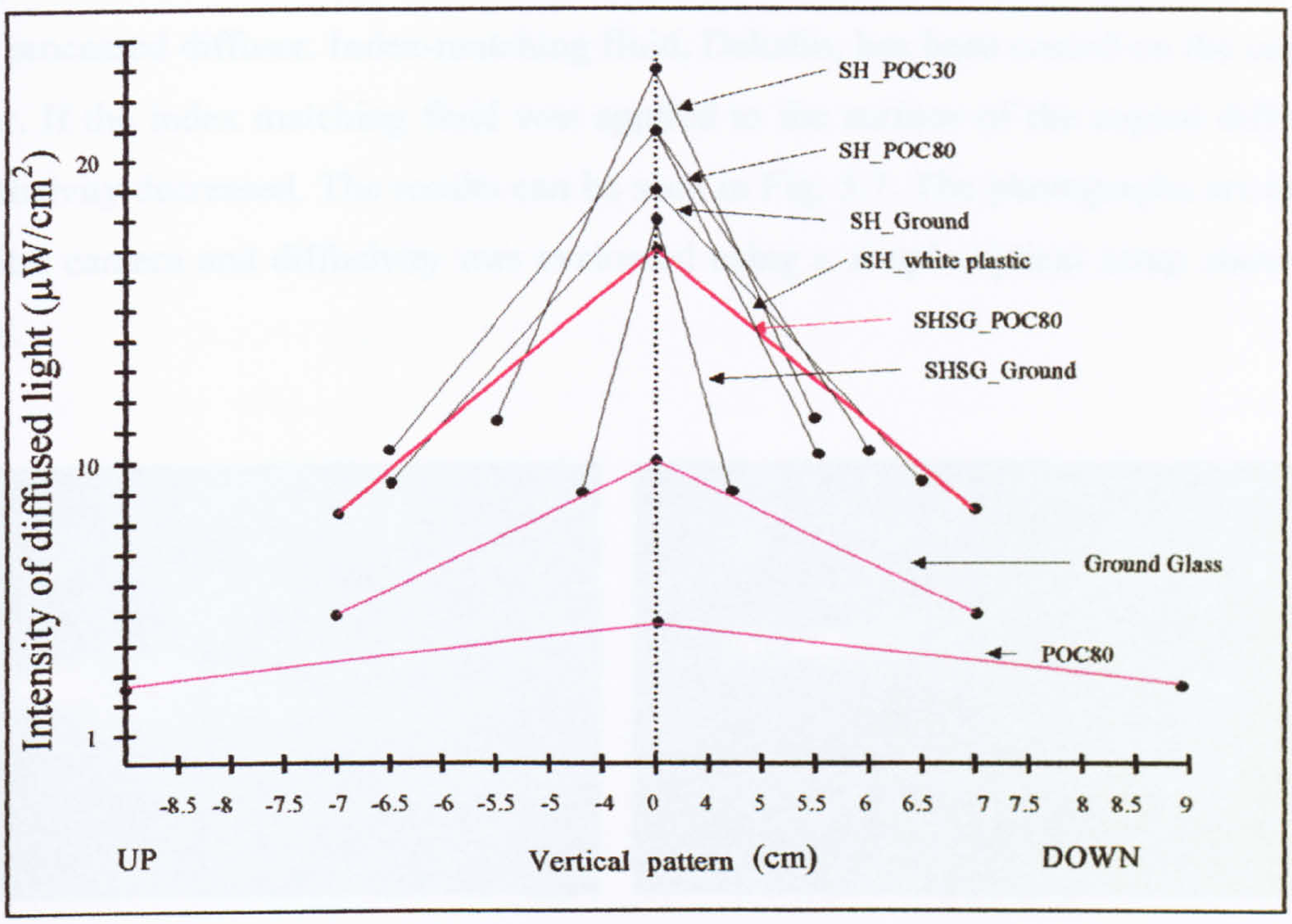
Table 5. 1 Typical samples prepared using various source diffusers and processing method

Samples	Distance to FWHM (cm)				Transmitted power ($\mu W/cm^2$)	Vertical angle (degree)	Horizontal angle (degree)
	Up	Down	Left	Right			
POC80	9.2	9.2	8.5	8.4	4.8	34.1	31.5
Ground glass	7.2	6.7	6	7.4	9.8	26.1	25.2
SH/POC30	5.5	5.2	5.5	5.5	23	20.2	20.8
SH/POC80	6.7	6.2	6	6	21	24.3	22.6
SH/GG	6.3	6.2	6.3	6.7	19	23.5	24.4
SH/Plastic	6.3	5.6	5	5.6	21	22.4	20.0
SHSG/POC80	7.1	7.1	7	7	17	26.6	26.3
SHSG/GG	4.5	4.5	4.6	4.6	18	17.1	17.4

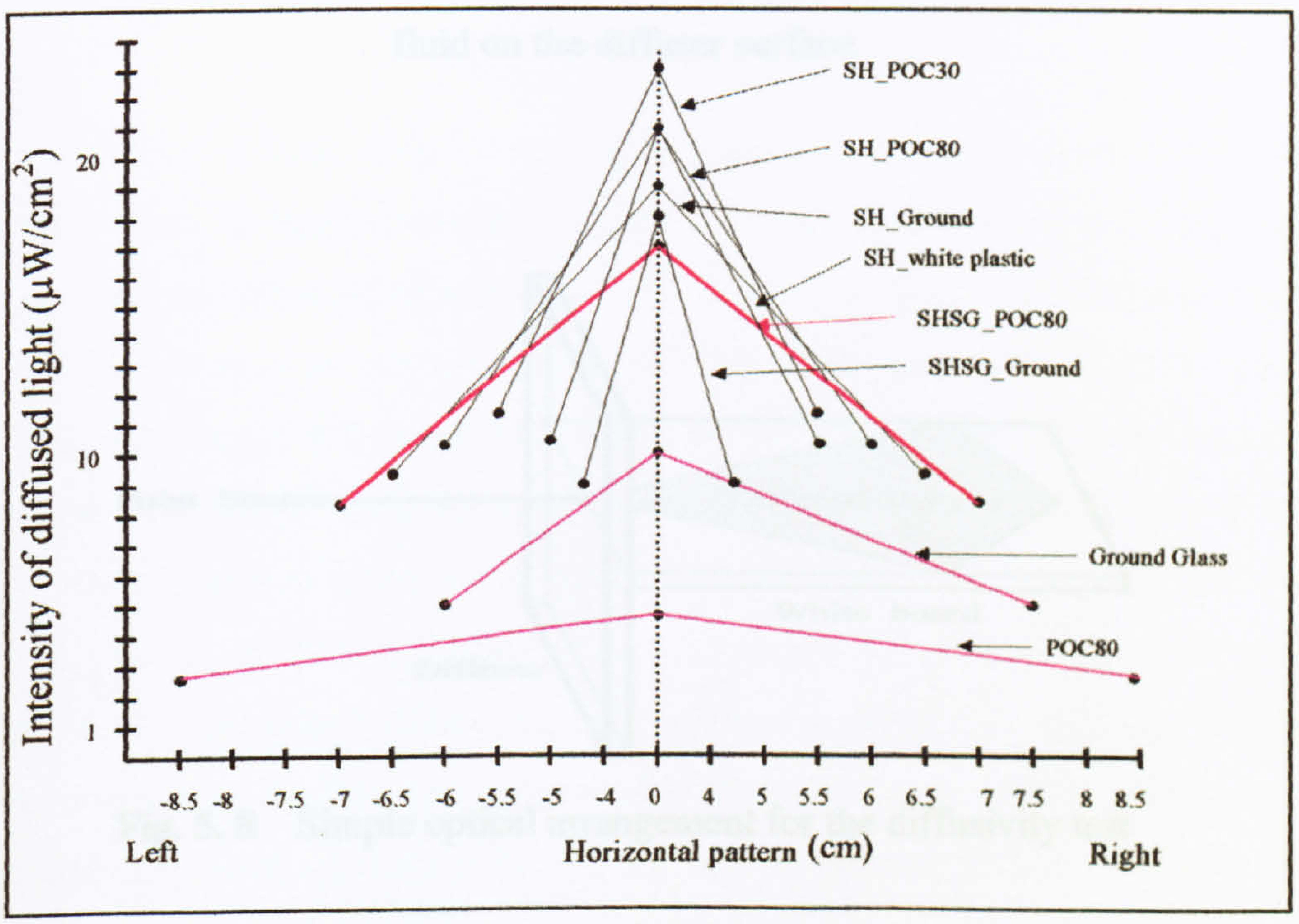
An important ingredient in this process is that diffusivity of source diffusers should be good, that is, the diffusing angle should be large enough to obtain better quality on copied diffusers. The important feature is that the polarization is preserved in the case of illuminating POC diffusers with coherent light. Polarization preservation is very crucial because the recording mechanism is similar to holographic recording.

5.3.2 Characteristics of SHSG Processed Diffusers

Since normal diffusers such as ground glass, opal glass and polycarbonate or polyethylene diffuser has random surface-relief structure, the scattering mechanism is not so powerful. But diffuser processed with the transmission SHSG process has texturized structure in the emulsion form by the microcavities and surface relief structure induced by the enlargement of microvoids during the SHSG process. That means that diffusers processed with the SHSG method have not only volumetric effect but also surface relief effect. The texturized structure provides the light path into the emulsion without obstructing light passes through the emulsion. This is why the diffusing angle of copied diffusers on SHSG emulsion approaches the value of 80% of the POC diffuser and the transmittance is three times higher than the POC diffuser.



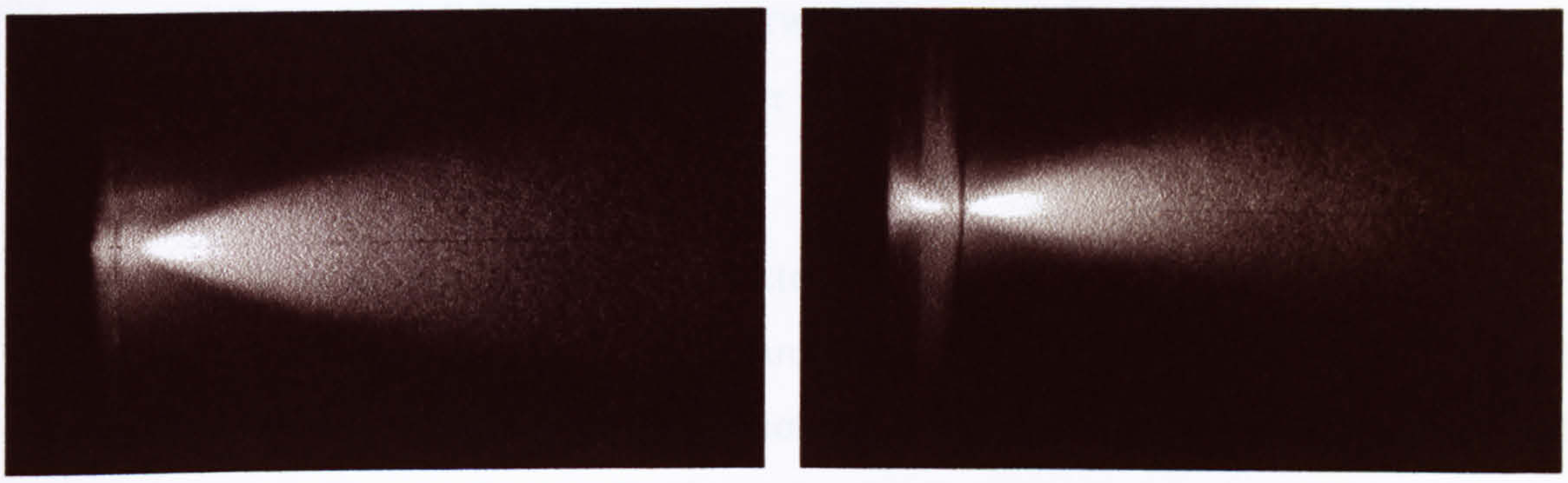
(a) vertical



(b) horizontal

Fig. 5. 6 Scattering characteristics of diffusers

A simple experiment has been performed to evaluate the surface relief effect of the SHSG processed diffuser. Index-matching fluid, Dekalin, has been coated on the copied diffuser. If the index matching fluid was applied to the surface of the copied diffuser, the diffusivity decreased. The results can be seen in Fig. 5.7. The photographs are taken by digital camera and diffusivity was evaluated using a simple optical setup shown in Fig. 5.8.



(a) before the application of Decalin (b)after the application of Decalin

Fig. 5. 7 Change in diffusing characteristic after the application of index matching fluid on the diffuser surface

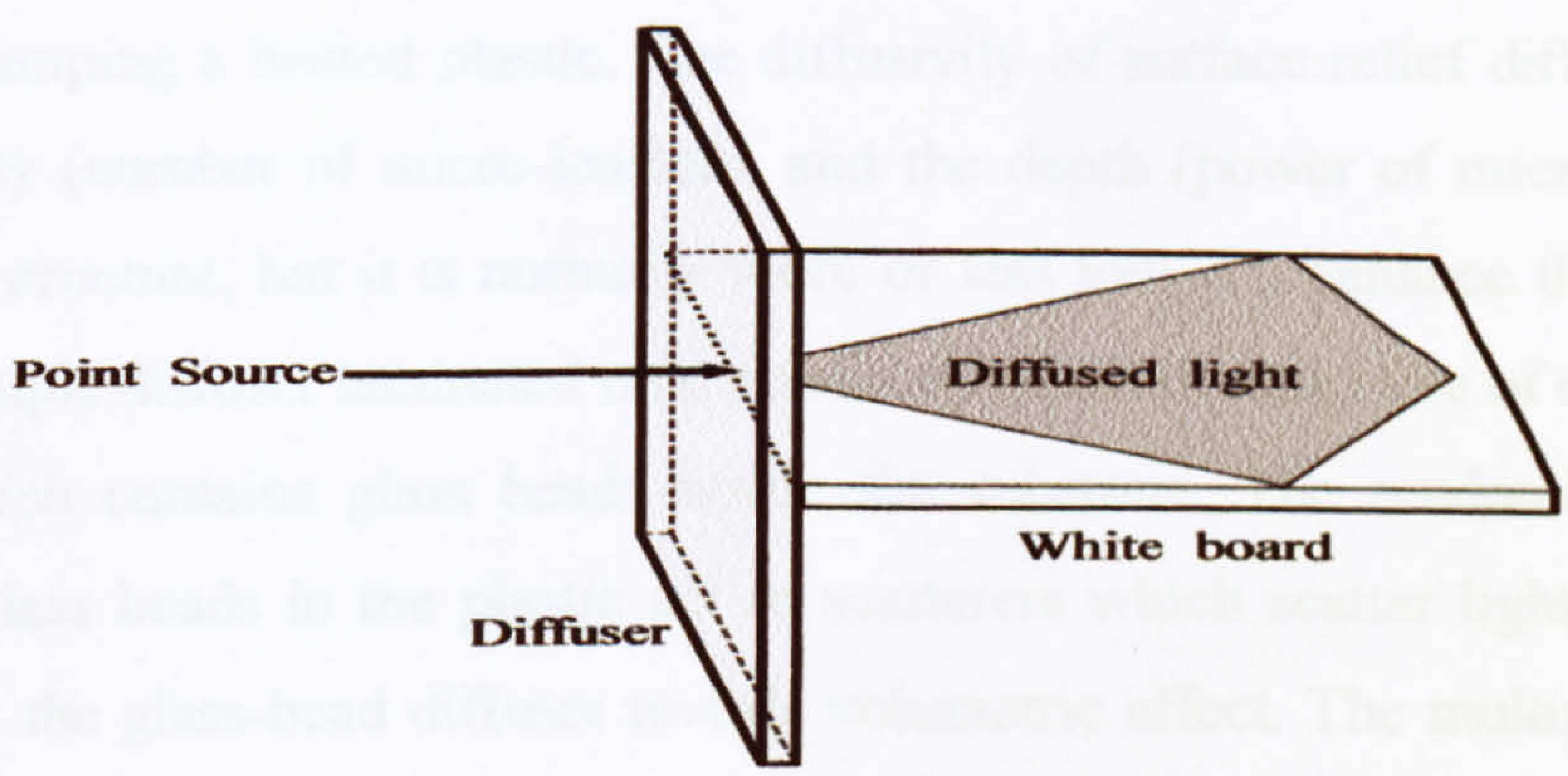
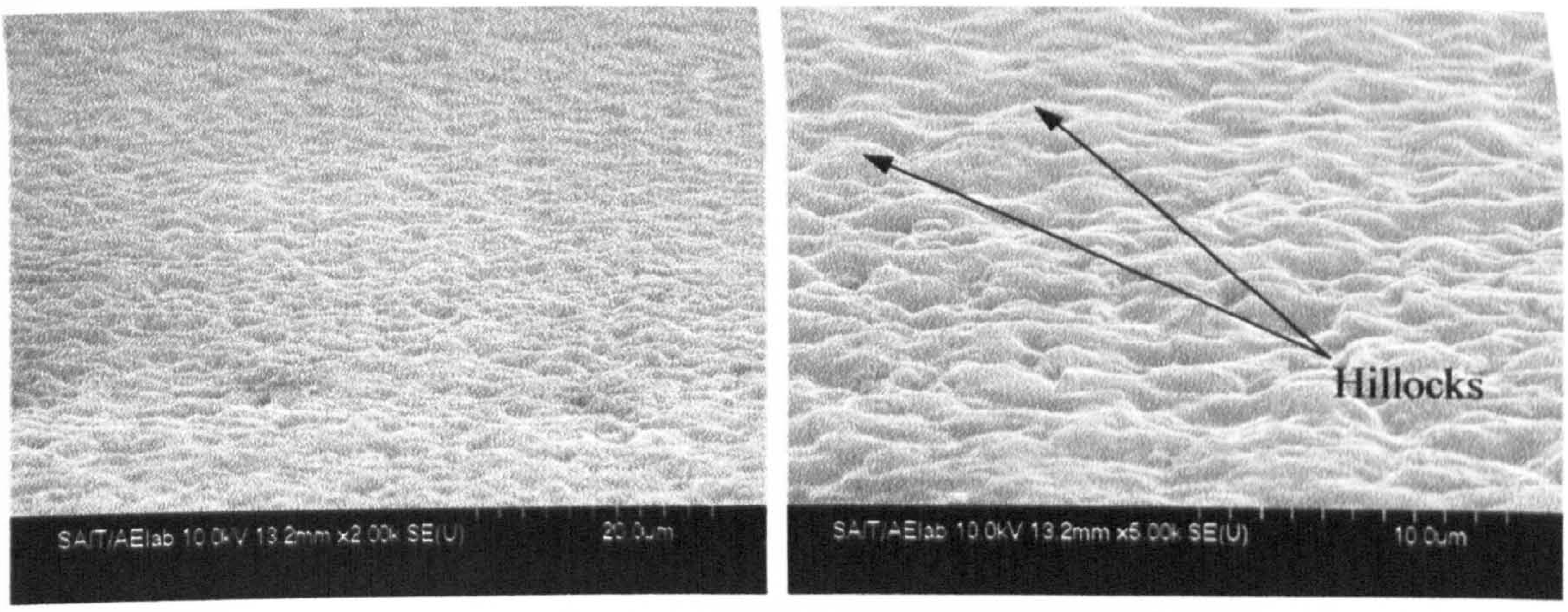


Fig. 5. 8 Simple optical arrangement for the diffusivity test

To investigate the microstructure of the diffuser processed with the SHSG method, scanning electron microscopy (SEM) photographs of the surface and cross-sectional structure were taken. The photographs of the copied diffuser surface, in Fig. 5.9, shows that many microscopic hillocks are formed on the surface which are distributed completely randomly and can be regarded as randomized micro lenslets. The non-periodic randomized structures help the light to be diffused in the arbitrary directions. Especially thousands of protuberances exist on the shell of micro-hillock which are formed by the enlargement phenomena in the final dehydration step. The protuberances on micro-hillock enhance the diffusivity of the copied diffuser and can be seen clearly in the photograph (Fig. 5.10) taken with higher magnification. In Fig. 5.10, the structural difference of diffuser surface between POC and SHSG diffuser is illustrated. The surface of the POC diffuser is smoother than that of the SGSH diffuser.

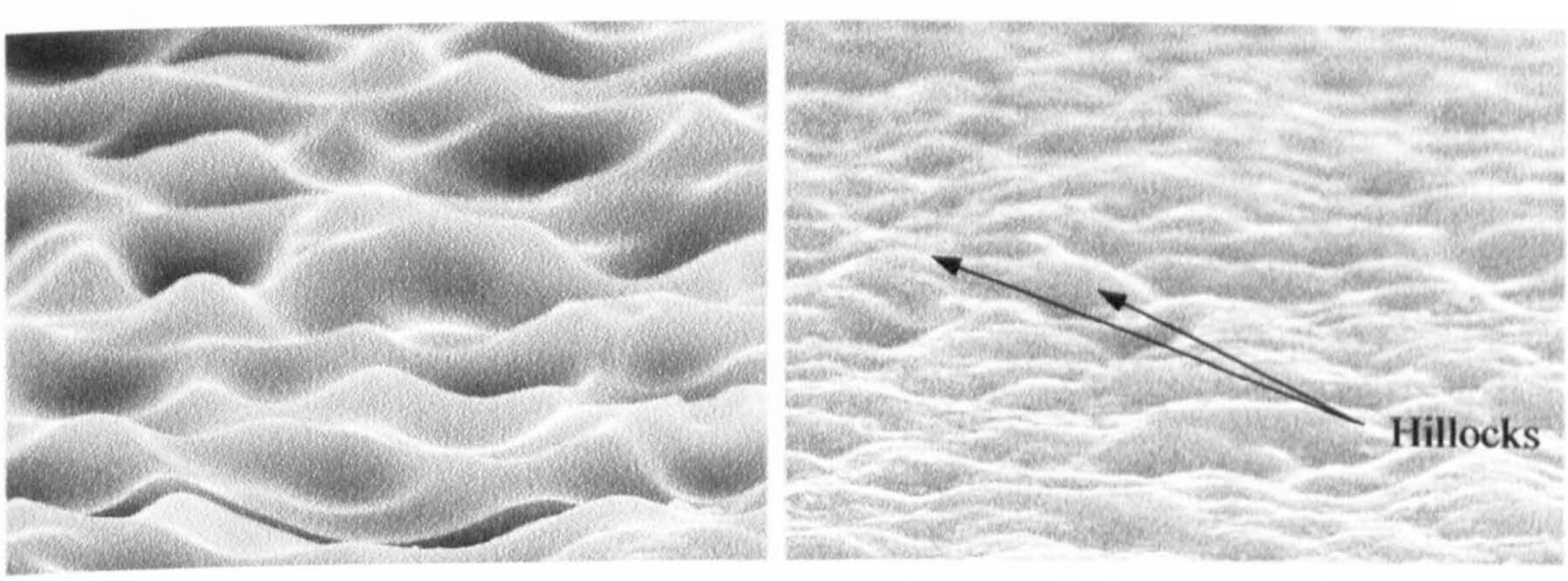
In Fig. 5.11, it is visible that microvoid structures are formed and some of them are arranged in a line which is inclined toward the micro-hillock. The thick arrows and parallelogram in Fig. 5.11 indicate the region of microvoid arrangement (the texturized structure). According to the results from the SEM investigation, it is clear that the diffuser manufactured using the SHSG process acts like as both plastic diffuser with scattering beads in it and embossed diffuser with surface relief effect.

Traditional diffusers have only surface relief effect since irregular rough (coarse) surface on a glass or plastic substrate is very easy to obtain simply grinding a glass surface or stamping a heated plastic. The diffusivity of surface relief diffuser depends on the density (number of micro-lenslets) and the depth (power of micro-lenslets) of microscopic structure, but it is normally more or less low. To enhance the diffusivity, they use multiple diffuser laminated onto a solid substrate or make use of special plastic substrate which contains glass beads inside the substrate. The randomly distributed (dispersed) glass beads in the plastic act as scatterers which scatter light into random direction, i.e. the glass-bead diffuser reveals volumetric effect. The multiply laminated diffusers usually have the thickness of several 100micrometer to several millimeters and the manufacturing costs of these diffusers are very expensive. But the volumetric and surface relief effects of the SHSG diffuser are enormous even though the thickness of the emulsion is only 7 μm. Thus a dual characteristic of the SHSG diffuser is very important for the practical application and manufacturing.



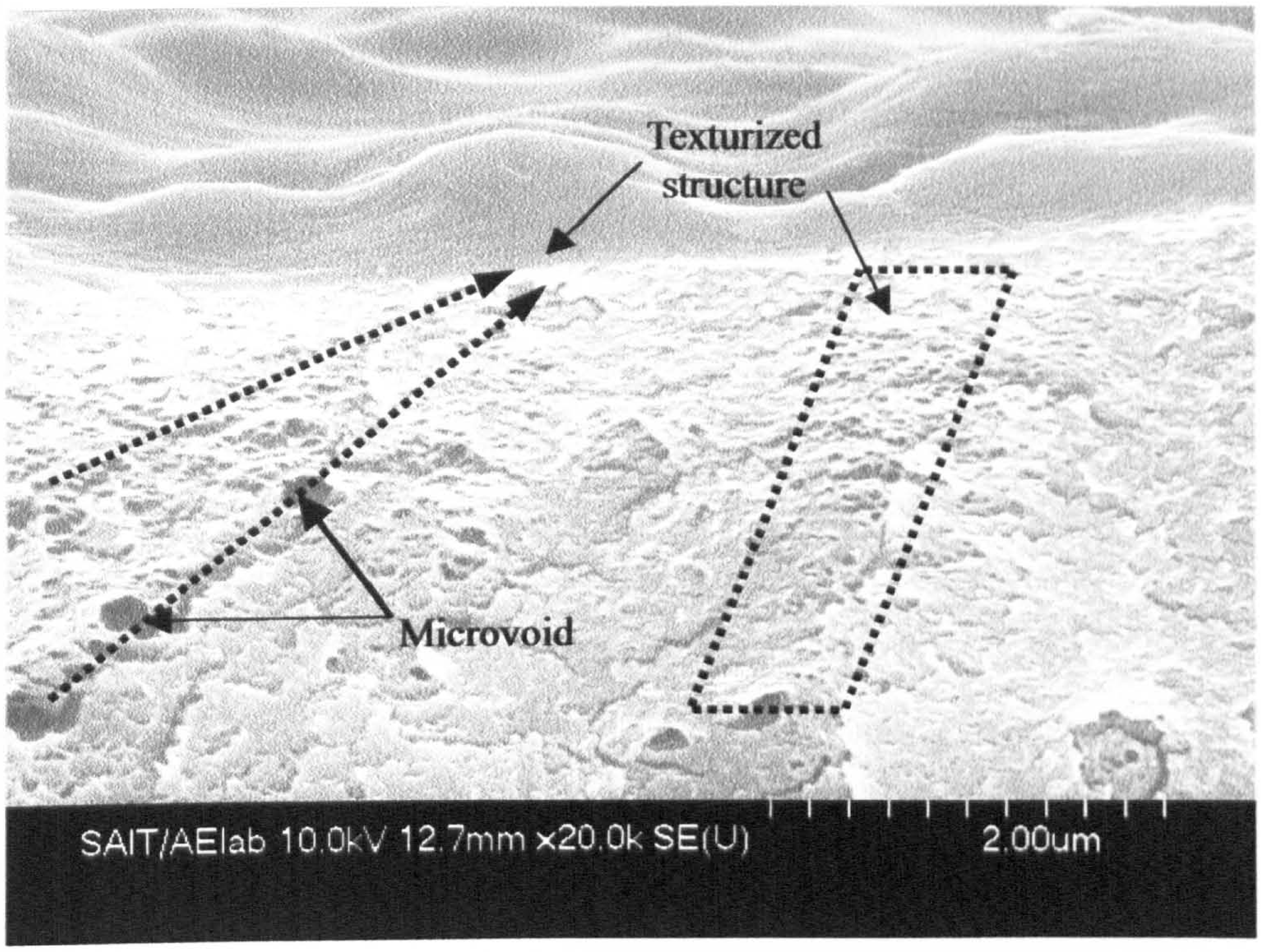
(a) lower magnification(2000X) (b) higher magnification(5000X)

Fig. 5. 9 SEM photograph (surface) of SHSG processed copied diffuser

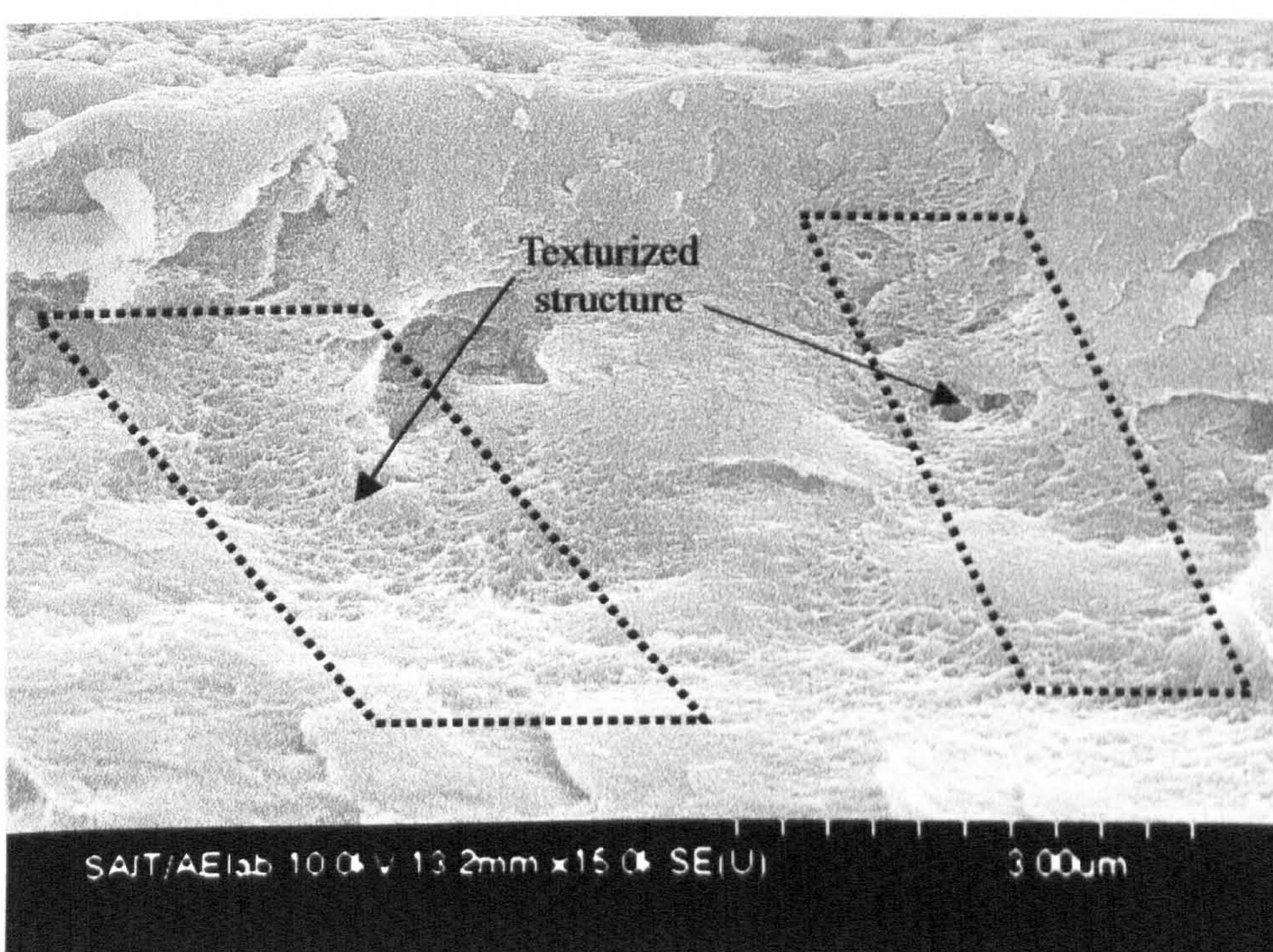


(a) POC diffuser (15K×) [5.5] (b) copied diffuser using SHSG (10K×)

Fig. 5. 10 Comparison between POC and SGSH diffuser



(a) higher magnification



(b) lower magnification

Fig. 5. 11 Cross-sectional microstructure of SHSG diffuser

5. 4 Fine Tuning of the Copy Process

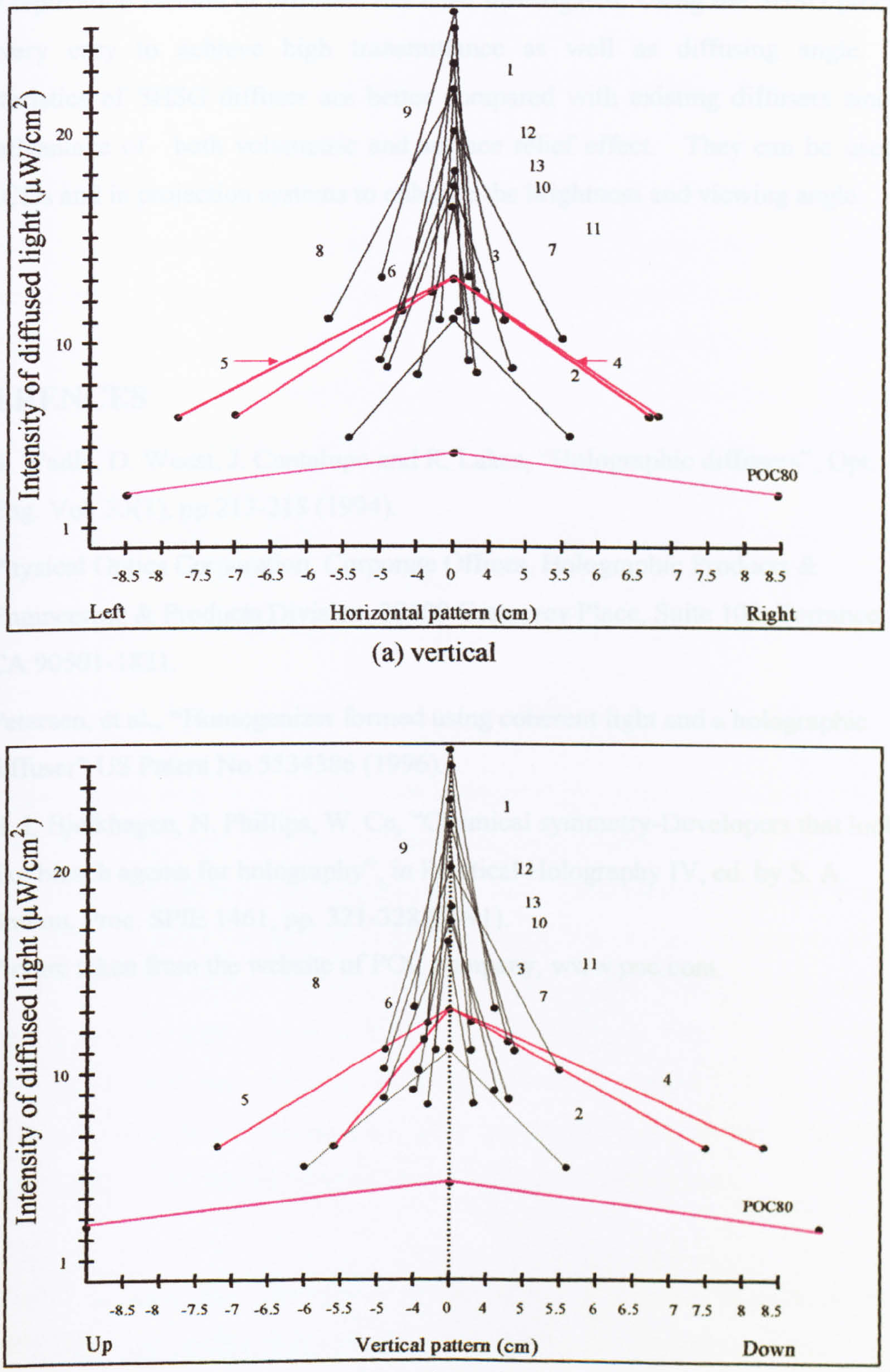
As mentioned above, it is obvious that a diffuser, which has a wide diffusing angle and preserves polarization, is adequate as the source diffuser for replication. The SHSG method is one of the best ways to replicate diffusers.

Another investigation to find the factors that influence the quality of copied diffusers has been performed. The main factors, which may have an influence on the diffusing angle and transmittance, are the spacing between the source diffuser and the emulsion plate, exposure energy in the recording step and the processing method of the copied plate after recording. Referring to the results explained above, it has been demonstrated that the SHSG method can enhance transmission while possessing a wide diffusing angle. Therefore the spacing and exposure energy have been changed to obtain the optimum condition for the replication process.

Typical experimental results for this investigation are listed in Table 5.2 and Fig. 5.12. The results show that sample No. 3(the lowest spacing and highest exposure energy) has the widest diffusing angle, when the diffuser is copied at L, spacing 5 cm and the exposure energy is around 2.0 mJ/cm^2. In this case, the characteristics of diffuser become better. Comparing the characteristic of the copied diffuser with that of the source diffuser, the source diffuser has the diffusing angle of 34° and transmittance of 4.5μW/cm^2. On the contrary, the copied diffuser has over 80% diffusing angle and more than three times higher transmittance. In conclusion, the SHSG method can be applicable to replicate diffusers with better quality than the source diffuser.

Table 5. 2 Typical results of experiments using variable spacing and exposure energy.

NO.	Spacing (cm)	Energy (mJ/cm^2)	Transmission power ($\mu W/cm^2$)	Diffusing angle (Vertical)	Diffusing angle (Horizontal)
1	0	2	22	12.9	13.5
2	5	1.5	13	26.1	25.7
3	5	2.5	13.2	27.5	27.2
4	15	1.5	17.5	17.8	18.2
5	15	2	22	18.2	18.9
6	15	2.5	25	12.9	13.3
7	25	1.5	18.6	12.9	14.4
8	25	2.5	20	19.5	19.5
9	30	2	11	21.7	20.8



(a) vertical

(b) horizontal

Fig. 5. 12 Scattering characteristics of copied diffusers processed with SHSG method

5. 5 Conclusion

A new replication method of diffusers has been investigated. Using the SHSG process, it is very easy to achieve high transmittance as well as diffusing angle. The characteristics of SHSG diffuser are better compared with existing diffusers since it takes advantage of both volumetric and surface relief effect. They can be used in TFT-LCDs and in projection systems to enhance the brightness and viewing angle.

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5.5 Picture taken from the website of POC company, www.poc.com.

Chapter 6

Extreme Angle Recording: Background and Methods

6.1 Introduction

In general, considerable space is necessary to record and replay HOEs and display holograms. Most holographic recording and replay systems require very complicated optical arrangements, to produce HOEs with high quality. Two methods for reducing the size of optical illumination system for the replay of HOEs are extreme-angle recorded HOEs and "Edge-Lit" HOEs. In these methods, it is comparatively easy to locate the light source at or near the edge of the substrate of the HOE. The advantages of extreme-angle recorded and edge-lit HOEs are compactness, minimization of diffractions by ambient light and use of wide range of light sources for illumination such as halide lamps or cold fluorescent light tubes with linear shape, light emitting diodes and laser diodes.

Development of the edge-lit HOEs was first introduced by Lin [6.1] and were published by several research groups such as Upatnieks [6.2, 6.3], Benton [6.4] and Phillips [6.5, 6.6] These groups preferred photopolymer since they could choose substrates that had adequate refractive index and laminated photopolymer film on that substrate to prevent total internal reflection at the interface. In spite of their efforts, edge-lit HOEs have not been widely used because of low efficiency and difficulty in large formatted HOEs. However, Phillips and his colleagues have applied small edge-lit HOEs to compact illuminator for finger print detection. [6.7] They have used photopolymers laminated on optical glass, which has similar refractive index with the photopolymer.

This chapter is about the applications of the SHSG processing to extreme angle recorded HOEs. The problems in recording these HOEs are explained and new work, which has been carried out as a part of the doctorate programme, is described. Section 7.3 describes the application of some of the methods developed in this chapter to an extreme-angle HOE for back-illumination of the LCDs.

6.2 Extreme Angle Recording

6.2.1 Problems of Extreme Angle Recording

As mentioned briefly in last section, there are several problems in recording edge-lit and extreme-angle HOEs. The problems are: total internal reflection between interfaces caused by steep angle of incidence, the necessity of polished edge on the substrate, the problem of illuminating the whole area of HOE through the edge and the determination of beam ratio between reference and object beam.

The difference in refractive indices of materials used in the recording is very important, because the illumination geometry in edge-lit HOE recording is an extreme condition. If the differences in refractive indices between them are too high, total internal reflection takes place at the interface. Therefore the substrate must be chosen to minimize the difference of refractive index. In addition, at least one edge of the substrate must be polished because light is introduced through it. It is very difficult to polish the edge of substrate after coating or laminating recording materials on the substrate. Thus the edge must be polished before introducing recording media onto it.

The uniform illumination of recording media seems to be difficult since the area of the edge is very narrow and limited compared with that of recording media. The determination of reference-object beam ratio is also difficult because of the strange geometry. Because of these problems, large formatted edge-lit HOEs have not been developed successfully.

6.2.2 Importance of Index Matching

Index matching in HOE recording is essential, in order to avoid noise such as unwanted interference patterns looking like wood grain, which can occur during extreme angle recording because of internal reflection. As well as reducing the effect of Fresnel reflections, index matching reduces the effect of phase distortion in film. [6.8, 9]

In general, dry gelatin has a refractive index of 1.54 and AgHal emulsion has an index of 1.53 to 1.64. This may be changed according to the processing, circumstance or manufacturer. As described previously, the main factor which causes noise during recording, is the refractive index difference between substrate and emulsion. The difference is about 0.1, which affects the quality of HOEs especially in extreme angle recording. To reduce unwanted reflection, we must find an index matching fluid with an index approximately halfway between 1.52(glass substrate) and 1.64(emulsion). It is very difficult to find such a liquid. Safety, chemical influence on the emulsion and substrate, and methods for removal of the liquid after recording must be considered. Commonly used index-matching liquids are white spirit, decalin, mineral oil and *p*- or *o*-xylene but xylene is a toxic solvent, decalin and mineral oil are too greasy and hard to remove after recording and white spirit has a refractive index which is too low.

In normal holographic recording, the refractive index of the fluid is not critical so that liquids with refractive index between 1.42 and 1.52 are acceptable. But in the case of extreme angle recording the refractive index of the liquid is crucial since the incidence angle of the reference beam is so high that internal reflection may take place at the interface such as liquid-substrate, substrate-emulsion, substrate-air and emulsion-liquid. The optical paths of lights in the edge-lit recording are shown in Fig. 6.1. As shown in Fig. 6.1, the reflected lights such as R_1, R_2 and R_3 should be minimized during extreme angle recording to obtain high quality and to avoid wood grains.

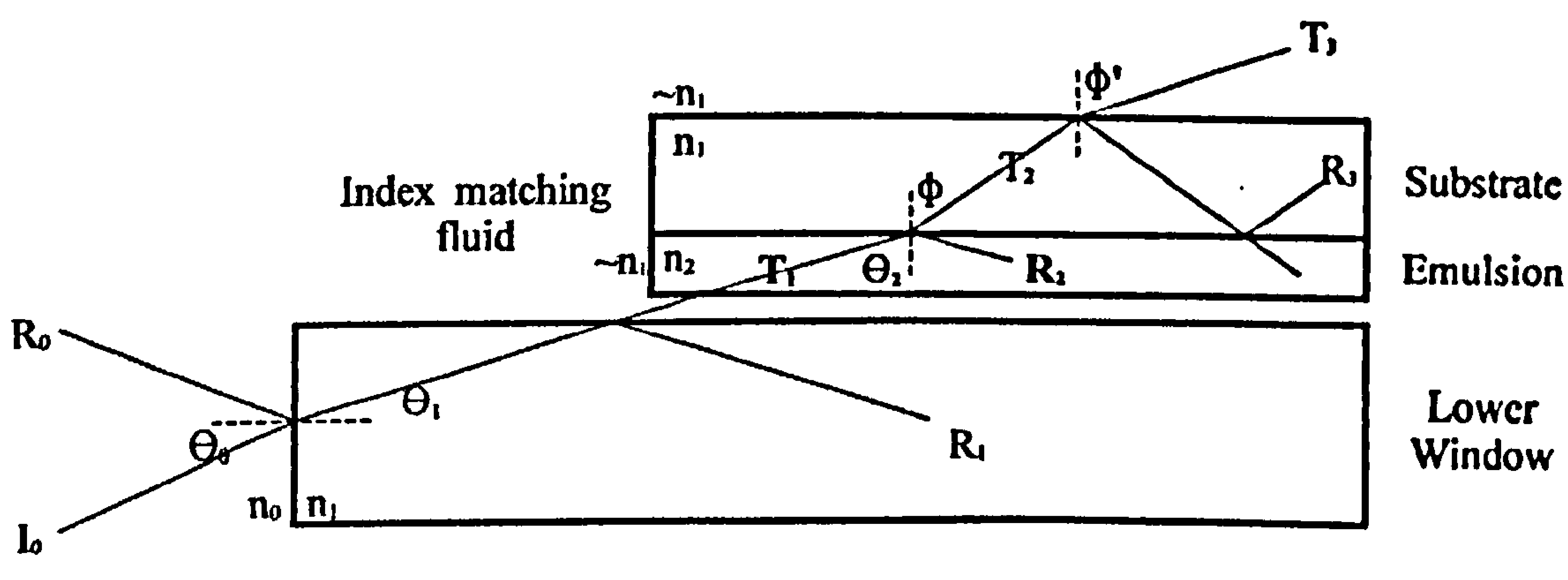

Fig. 6.1 The ray diagram shows the paths of lights in the edge-lit HOE recording

6.3 The New Approaches for Extreme-Angle HOEs

6.3.1 Cocktail of Index Matching Fluids

We have reviewed previous work and the nature of the problem: now we go on to describe the new approach carried out in this work. As we saw in the last sections, appropriate index matching fluid and optical arrangement are necessary to get rid of wood grains or unwanted fringes in extreme angle recording. As for the AgHal holographic plate, the refractive index of liquid should be 1.57, which is the middle value of the refractive index between emulsion and substrate. Since it is very hard to choose index-matching fluid that has refractive index higher than 1.52, a cocktail of index-matching fluids mixed with solvent such as isopropanol (n=1.3614) or ethanol (n=1.36) is used. The desired value refractive index can be obtained easily by mixing two different liquids, giving an index calculated according to

$$\frac{P_1}{100}=\frac{n_m-n_2}{n_1-n_2}, \qquad (6\text{-}1)$$

where P_1 is the volume percent of liquid 1, n_1 is the refractive index of liquid 1, n_2 is that of liquid 2 and n_m is that of the mixture. As an example, about 70 volume percent of bromo naphthalene (n=1.658) has been added to 100 volume percent of isopropanol to obtain the refractive index value of 1.57.

6.3.2 Determination of Beam Ratio

The beam ratio (OR ratio) between the reference beam and the object beam is quite important to get maximum diffraction efficiency and minimum signal-to-noise level. In the case of recording edge-lit HOEs and extreme angle HOEs, the determination of OR ratio is very difficult because of the strange geometry of recording. To determine the OR ratio more accurately, a method using illuminometer has been found. For the method, a fluorescent film or a wide-angle diffuser coated (laminated) on a substrate was necessary. The substrate should have exactly same size and shape as the plate used for the real recording. Placing the substrate at the position of recording, a half of each reference and objective beam was blocked out as shown in Fig. 6.2. Then four zones with different brightness appeared on the substrate surface, which were very clearly seen. But it was very difficult to measure the exact value of illumination. To measure the luminousintensity of each zone, normal spot-illuminometer was employed. The spot-illuminometer is often used in the field of photography to measure the brightness of the object.

To control OR ratio, we could measure the luminousintensity of zone ② and ③, and adjust beam splitter. In general, the intensity measurement of the reference beam is not easy since the shape of the reference beam is like narrow linear light source. On the other hand, it is very easy to measure the intensity of the object beam using laser power meter because the object beam normally illuminates the recording plate with a right angle. Thus total power, I ($=I_O+I_R$) should be calculated using the assumption that the intensity (illumination power) is proportional to the luminousintensity.

$$I_R=(L_R/L_O)\ I_O \tag{6-2}$$

where L_R is luminousintensity of the reference beam and L_O is that of the object beam.

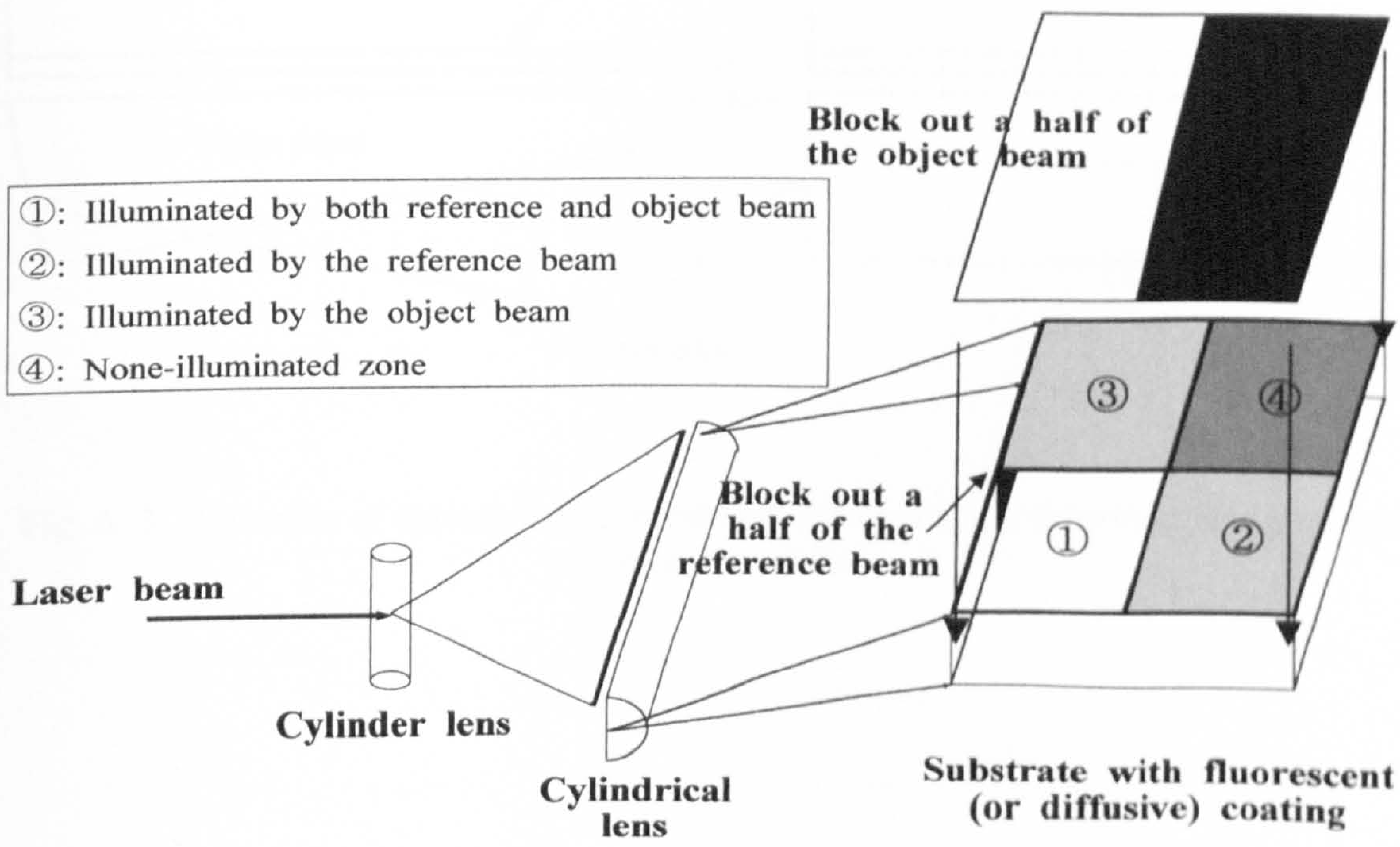

Fig. 6. 2 Determination of beam ratio in the edge-lit recording

6.3.3 Recording Method of Extreme Angle HOEs

An alternative method of recording extreme angle HOEs is using wedge prism or optical flat with considerable thickness and polished edge as shown in Fig. 6.3. The merit of using a wedge prism or optical flat is the convenience in optical arrangement for the recording and replay of recorded HOEs. In the recording step, the reference beam comes through the polished edge at a certain angle bigger than 85° to the substrate surface. Index matching fluid with the refractive index of 1.57 has been applied to the interface of the wedge prism or optical flat and the holographic plate to avoid wood grains.

As explained previously, a homogeneous illumination is very important in the extreme angle recording to obtain uniform characteristic of the HOE. Thus two methods for producing uniform sheet beam have been used to make HOEs. Fig. 6.4 shows the optical arrangements that generate sheet beam incident at a steep angle for the illumination of plate from the edge.

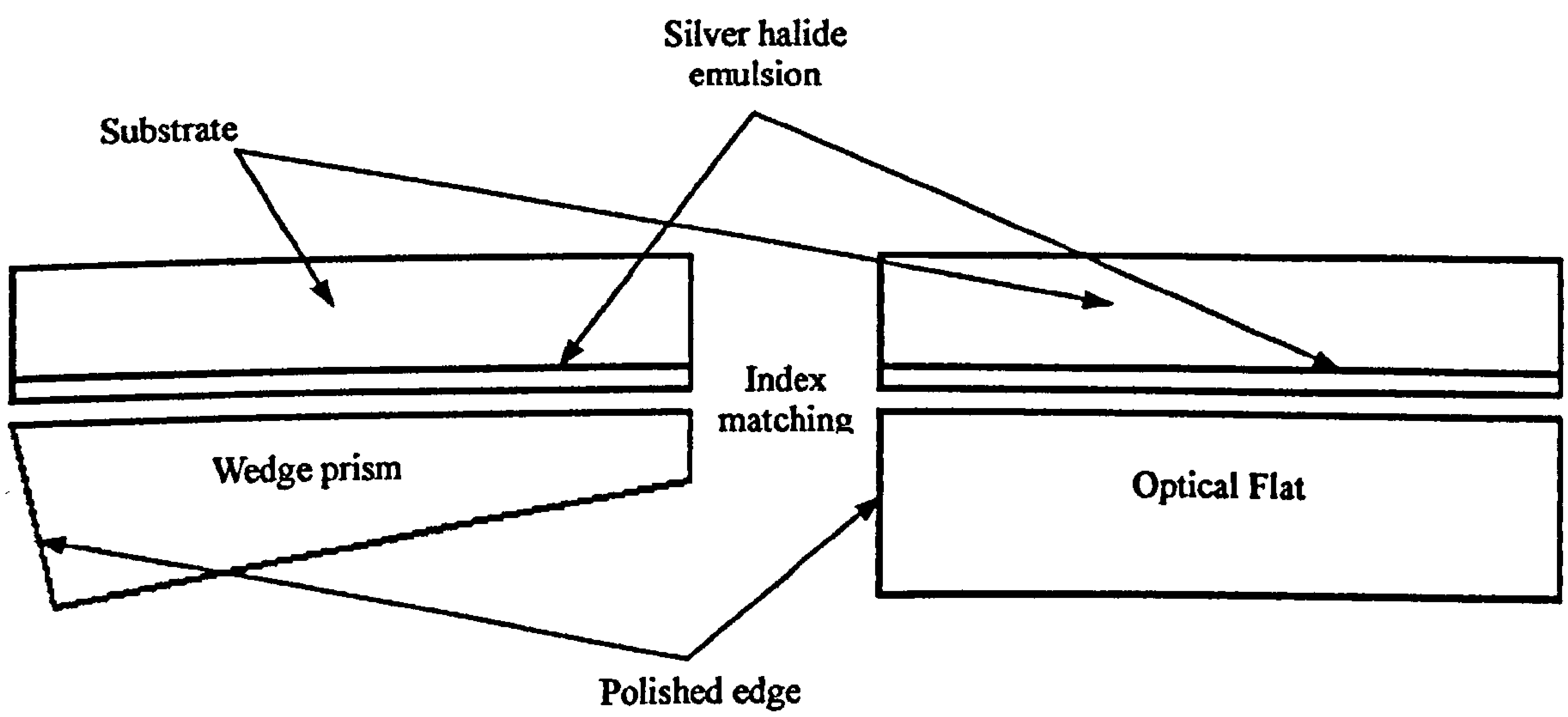

Fig. 6. 3 Example of optical arrangements for extreme angle recording using wedge prism or optical flat

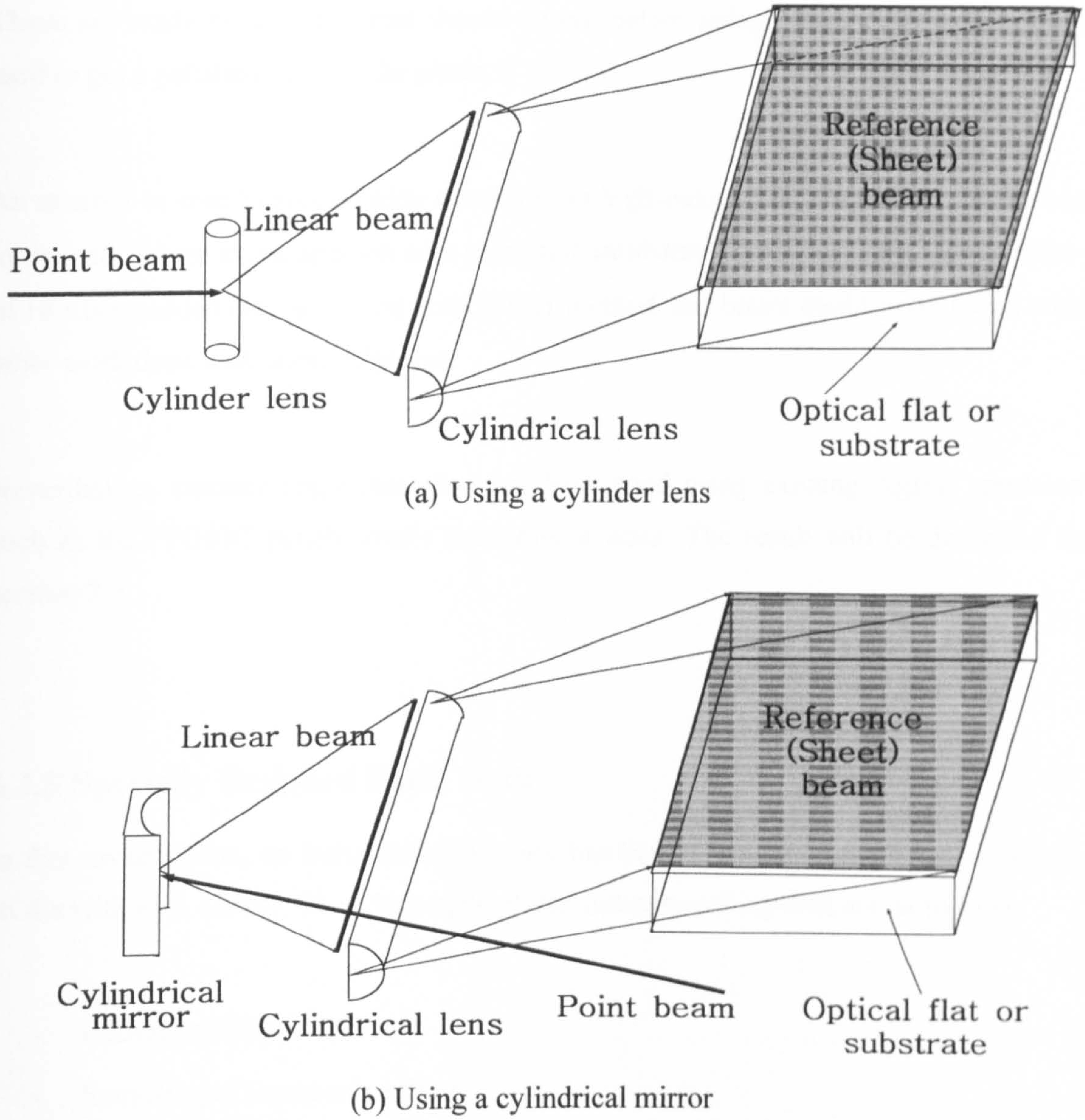

Fig. 6. 4 Example of optical setup to illuminate substrate at an extreme angle

6.3.4 Extreme Angle HOEs Recorded in SHSG emulsion

In this investigation, several approaches have been considered to scale up the size of edge-lit HOEs using AgHal emulsion. It appears that better results may be obtained by using AgHal emulsion coated on a glass with same refractive index as AgHal emulsion, that is around 1.64 and with polished edge. Unfortunately however, almost all AgHal emulsion are coated on ordinary soda lime glasses that have refractive index of 1.52. These are ready made plates that should be cut before using. After cutting, it is very hard to get a polished edge on the plates.

An attempt to coat high-resolution emulsion on high-index glass should be carried out in the near future in cooperation with glass and emulsion manufacturers since the edge-lit HOEs recorded and processed with SHSG method had better quality compared with other work done with photopolymers.

Nevertheless, extreme angle recording has been tried using existing AgHal emulsion such as the PFG03C panchromatic holographic plate. The result will be described in section 7.3.

6.3.5 Specially Designed Fluid Tank

In this investigation, an index-matching tank has been specially constructed to record HOEs with high quality. The advantages of this index-matching tank are as follows:

- Reproducibility of HOEs,
- Recycling of liquid using filter,
- Safety (the tank could be used as a fully the enclosed system with ventilation),
- Preventing the generation of air bubbles,
- To arrange the optical the optical path, one may simply tilt the tank.

In the index-matching tank shown in Fig. 6.5, both optical windows made from optical BK7 glass have been employed to avoid ripples on the top of the liquid and stabilize motion of liquid quickly.

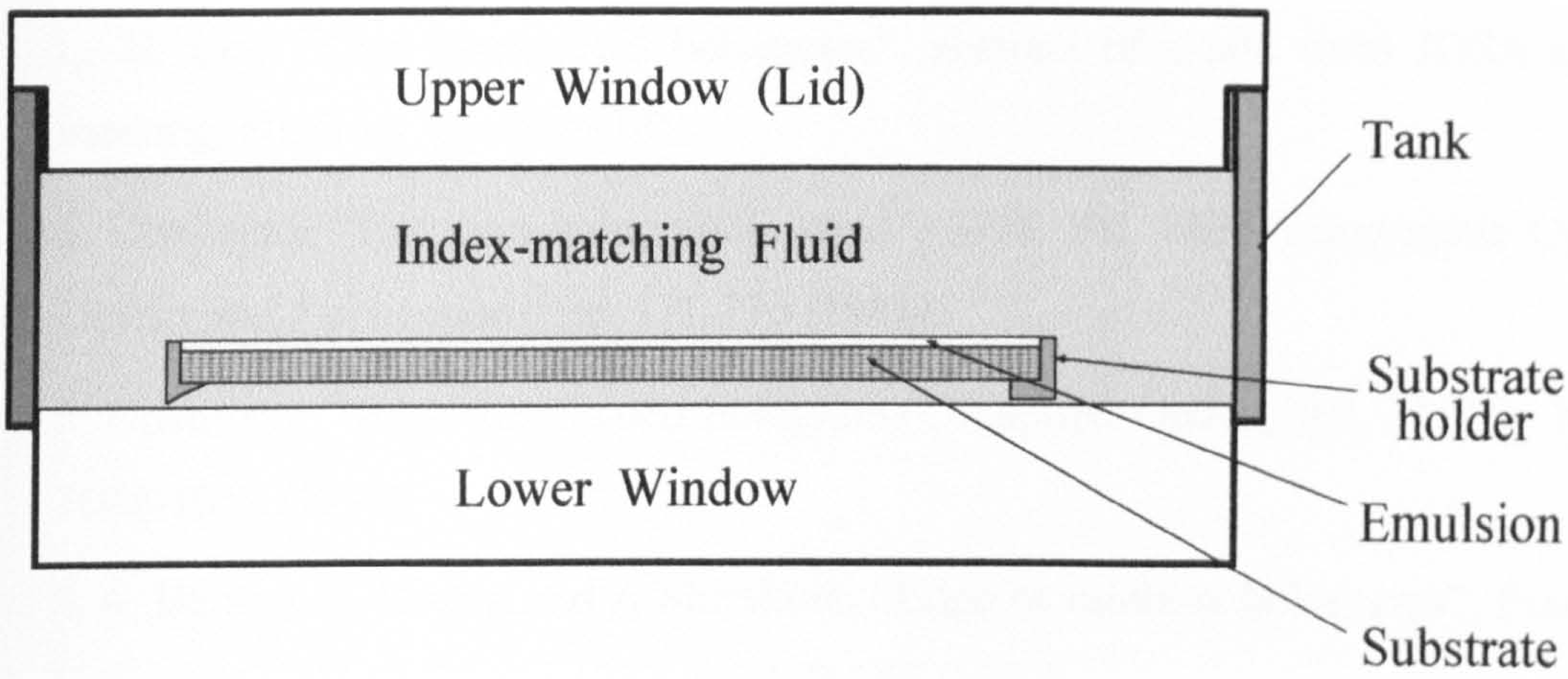

Fig. 6. 5 Index matching tank with two windows (top and bottom) for extreme angle recording

6.4. Conclusion

The recording method of edge-lit and extreme angle HOEs has been reviewed. Edge-lit and extreme angle HOEs can be applied to the compact illumination system such as LCD backlight.

New approaches for the recording of extreme angle HOEs are investigated to solve the problems which may occur during recording step. Alternative recording method called extreme angle recording has been examined, which was found to be more practical in use and readily applicable to the LCD backlight or compact illumination systems. In addition new apparatus, that is, index-matching tank has been constructed and used to make holographic reflector which can be adapted to the LCD backlight. The result will be described in the Section 7.3.

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Chapter 7

HOEs for Display Application

7.1 Introduction

Novel processing schemes of AgHal emulsion have been described from Chapter 2 to Chapter 4. The new processing methods are suitable for transmission and reflection HOEs and both monochrome and colour HOEs with high quality can be produced using these methods. As a consequence, the development of the SHSG process makes it possible to achieve very high efficiency over the entire visible spectrum. Therefore various designs for new holographic devices, which were hard to manufacture using former materials or processes, become more practicable. The most feasible field of application of the new SHSG method may be the development of high quality HOEs applied to modern optical systems to be used for displays.

Nowadays the applications of HOEs become more popular since the characteristics of recording materials has been improved gradually and there are plenty of demands in the market to produce more compact and complicated optical system that can not be manufactured using traditional optical components. HOEs have enabled the production of optical systems with lower cost, compactness and high quality. HOEs can provide unrivaled features mentioned previously, which can be applied to laser optics, optical filters, optical communications, display devices and optical electronics. [7.1]

Traditional optical elements change optical wavefronts by means of refraction and reflection. On the contrary, HOEs are kind of optical elements, which diffract incident light to a certain direction or make any shape determined by the recording process, that is, the optical geometry or arrangement for recording HOEs. One of the most important advantages is independent of the substrate's geometry or shape, i.e. HOEs can be made on a curved substrate or on any other extraordinary shape. In addition, HOEs can be designed and produced to act as multiply combined optical elements.

In this chapter, several applications of HOEs processed with the SHSG method have been investigated. Especially, HOEs for LCDs applications such as holographic reflectors for reflective LCDs and LCD backlight as well as illumination of HOE have been described.

7.2 Reflective LCDs; Multiply Stacked Holographic Reflectors

7.2.1 Reflective LCDs

Recently, compact mobile electronic appliances like as palmtop PCs, HHPs (hand held phones) and PDAs (personal data assistants) have been introduced in the market. These mobile electronics make use of LCD panels with several illumination systems such as black and white reflective panels, transreflective panels and colour reflective panels, which have more than 4 grayscales (64 colours).

Unfortunately however, the quality of images displayed on those panels is still low. They typically suffer from low brightness and lack of colour representation. In order to achieve high quality in display panels, improvements of characteristics in grayscale, colour representation, efficiency of light and contrast ratio are necessary. In these characteristics, the improvement of reflective efficiency i.e. the brightness is the most important. The power consumption is also important for the mobile applications. The backlight unit in the LCDs consumes the most of battery power.

In ordinary transmission-LCDs, two polarizers (polarizer at back and analyzer at front side) have been applied. This structure makes it easy to control the grayscale but it has the drawback of low brightness because the transmission of a polarizer is less than 45%. Recently there are several reflective LCDs developed using one polarizer or no polarizer. PDLC (Polymer Dispersed Liquid Crystal) [7.2] and PCGH (Phase Charge Guest Host) mode [7.3] are two examples in which there are no polarizers used in the display system. Because PCGH mode has strong hysteresis in the driving mechanism, it is difficult to control the grayscale. In PDLC mode, liquid crystal is dispersed from the mixture of monomer and liquid crystal using thermal reaction, UV exposure or solvent reaction.

The advantage of PDLC is that grayscale is easily controlled, that is, it is easy to represent full colour, but disadvantages are that contrast ratio is lower than normal LCDs and driving voltage is high. Recently ECB (electrically controlled birefringence) mode [7.4] has been adapted in reflective LCDs. In ECB mode, the loss of light efficiency has been reduced using one polarizer and two complementary colours like cyan and red instead of red, green and blue.

The reflective LCDs developed until now have employed a reflector or reflecting structure inside or behind the LCD panels. In these cases, because the light passes through the colour filter twice and the transmittance of colour filter is less than 90% for specific wavelength and less than 35% for white light, brightness may be reduced. [7.5, 7.6]

Almost all reflective LCDs developed most recently have utilized metal thin film such as aluminum with high reflectivity, which play roles as pixel electrode and reflector. These thin film reflectors have rugged surfaces in order to enhance the viewing angle by reflecting light from off axis directions or angles effectively. The properties of the reflectors are important for the viewing angle and reflectivity. For the ideal reflector, reflectivity is distributed uniformly up to a certain viewing angle, and beyond those angles reflectivity should be reduced dramatically. On the other hand, if the brightness has been enhanced, the viewing angle may be reduced and the dependence of brightness according to viewing angle should be deepened. Especially, in case of using colour filter, since specific wavelength within the visible spectrum is effective, other range of wavelength should be consumed unnecessarily.

7.2.2 Holographic Reflectors for Reflective LCDs

Some efforts [7.7-9] have been devoted to the use of HOEs as reflectors and colour representing filters because HOEs have the properties of colour representation, wavelength selectivity and convenience in design of optical structure. The efficiency of HOE reaches maximum value at the Bragg condition, otherwise light beam pass through the HOE without diffraction. Therefore HOEs are usable only under the correct illuminating conditions.

In order to overcome this weak point of HOEs and to apply reflection HOEs to reflective LCDs, the feasibility of multiply stacked HOEs are suggested and investigated. The purpose of this investigation is to improve the brightness and the quality of colour representation. Because HOE diffract light beam with a specific wavelength incident at the Bragg angle and transmit other wavelengths, the brightness can be improved by recycling transmitted (non-diffracted) beams using multiply stacked HOEs that diffract light beams with different wavelengths. As mentioned previously, reflective LCDs using colour filter or reflecting methods waste at least two thirds of the incident light. On the other hand, multiply stacked holographic reflectors made the advantage of recycling wasted light. This scheme should impact greatly on the light efficiency of reflective LCDs.

A schematic diagram of this idea is shown in Fig. 7.1. The pixel arrangement in this diagram is for typical LCDs. The triple stacked reflector at the first pixel to the right works in such a way that the first reflector diffracts red light at a certain angle (which is nearly perpendicular to the panel surface) and transmit green and blue light. The second reflector diffracts green light at an angle, which is a function of pixel pitch and thickness of reflector and transmit blue light. The angle ϕ can be expressed by the equation,

$$\phi = \tan^{-1}(d/t), \tag{7-1}$$

where Φ is replay (reflection) angle of 2nd and 3rd reflector, d is pixel pitch, t is thickness of individual reflector (spacing between reflectors) and θ is replay(reflection) angle of first reflector. Similar to the second one, the third reflector diffracts blue light at the same angle. The following pixels are working exactly same way according to the wavelength.

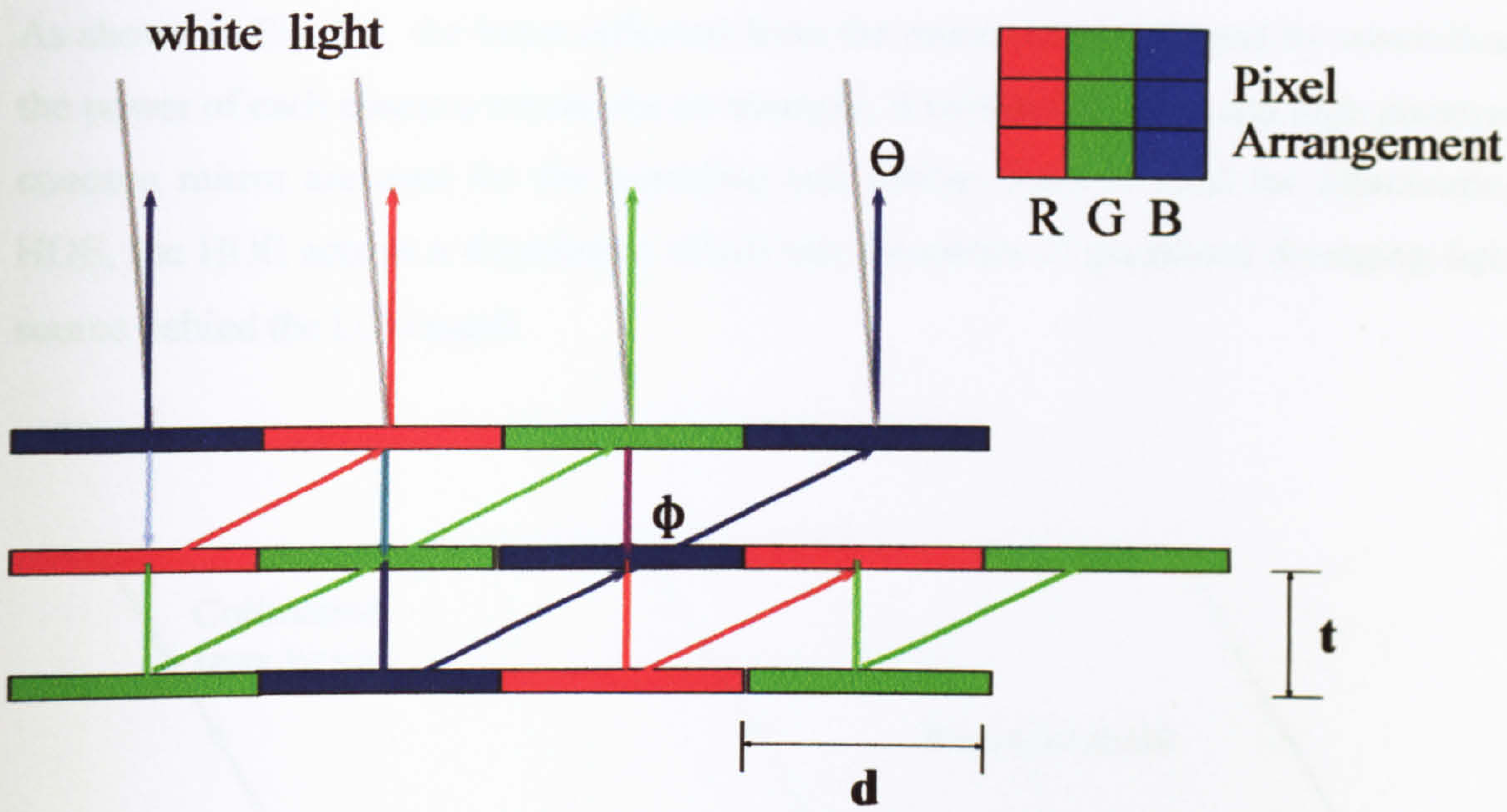


Fig. 7. 1 Schematic diagram which shows the concept of triple-stacked reflector.

7.2.3 Recording of Holographic Reflectors

The recording of those reflectors described above is quite difficult because of the colour variation of normal holographic reflector according to the viewing angle. This phenomenon is well known drawback of colour HOEs. Another difficulty arises from the recording of pixellated array of HOEs.

To solve this problem, a recording method for the first pixellated master HOE (reflector) in Fig. 7.1 has been introduced, which is shown in Fig. 7.2, 3, 4, 5 and Fig. 7.6. In this method, a pixellated precision mask and micro-structured concave mirror are used. To record only one colour pixel at once, the mask blocks two pixels nearby, which will represent different colours. After the first recording, mask has to move one pixel width and record the next colour pixel sequentially. For this recording method, a mask with the same patterns same as the LCD pixels and a mask aligner to move the mask precisely are necessary.

The role of the micro-structured concave mirror is that it directs incident beam toward the recording plate and shapes the beam, which illuminates the plate as an object beam. As shown in Fig. 7.3, the beam reflected from the mirror can be shaped by controlling the power of each concave mirror. As an example, if collimated beam and high powered concave mirror are used for the recording and similar beam is used for illuminating HOE, the HOE acts as a illuminator which has thousands of pixellated diverging light source behind the LCD panel.

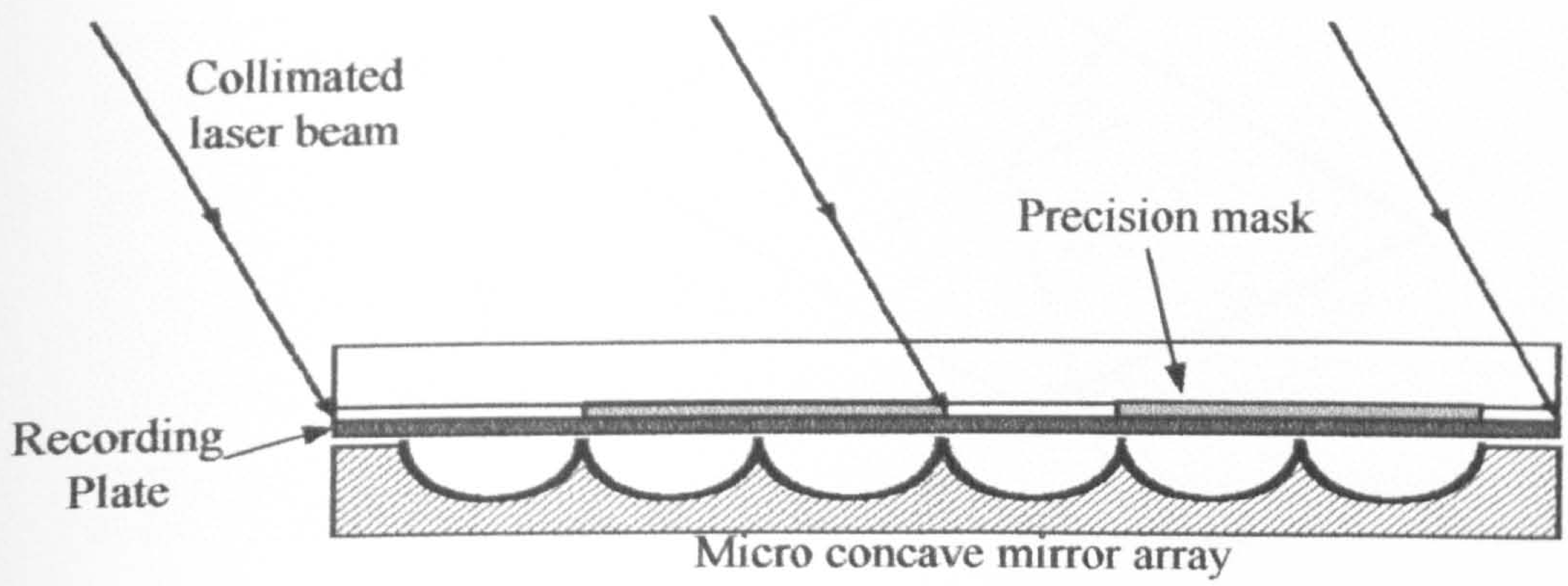


Fig. 7. 2 Schematic diagram shows the recording of first reflector

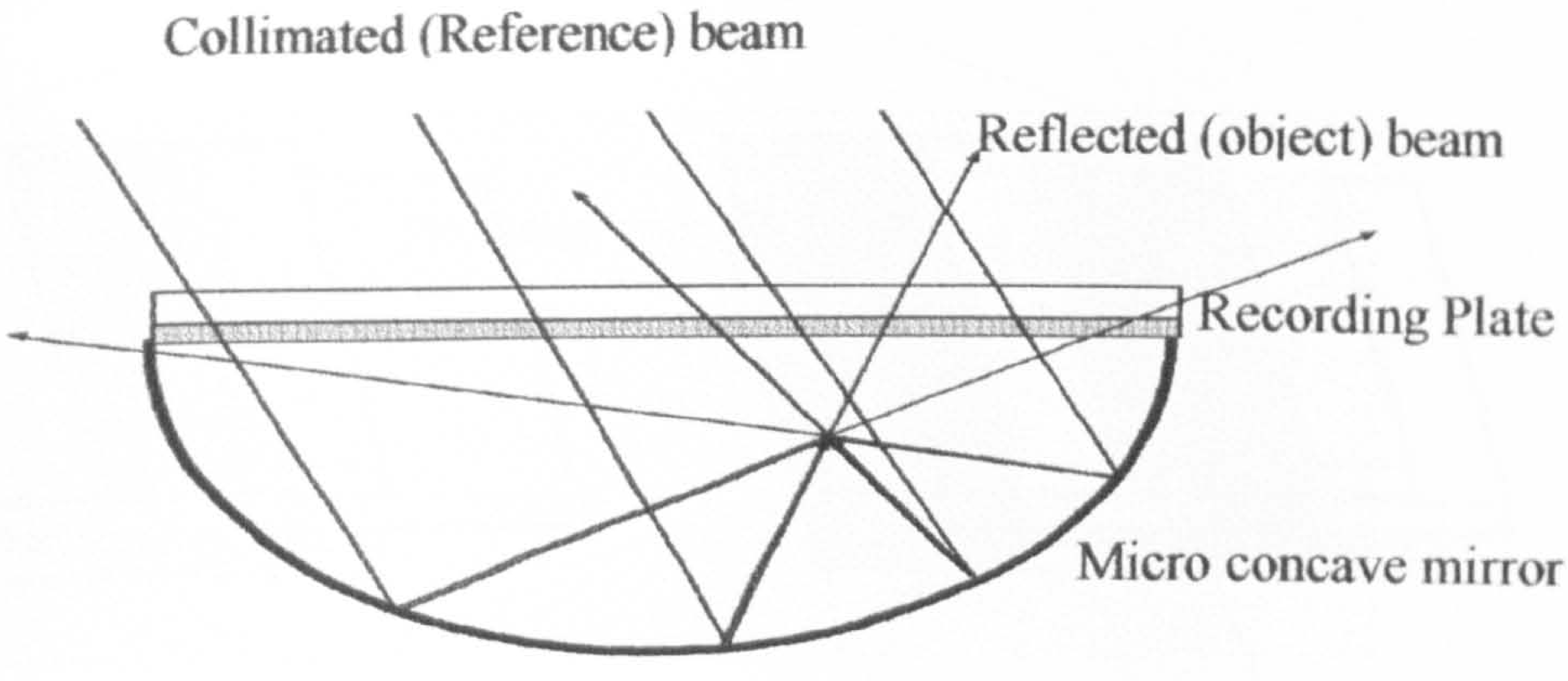


Fig. 7. 3 Schematic diagram shows beam paths for the individual pixel

The off-axis recording methods of the second and third reflector are shown in Fig. 7.4, 7.5 and Fig. 7.6. In Fig. 7.4, the reference beam parallel to the y-z plane illuminates the plate with an angle of θ and object beam parallel to the x-y plane comes from backside of the plate with an angle of ϕ. After the first exposure to record red reflector, the mask has to be translated to an extent of one pixel pitch, d. Then second (green) and third (blue) pixels are recorded successively as shown in Fig. 5.21.

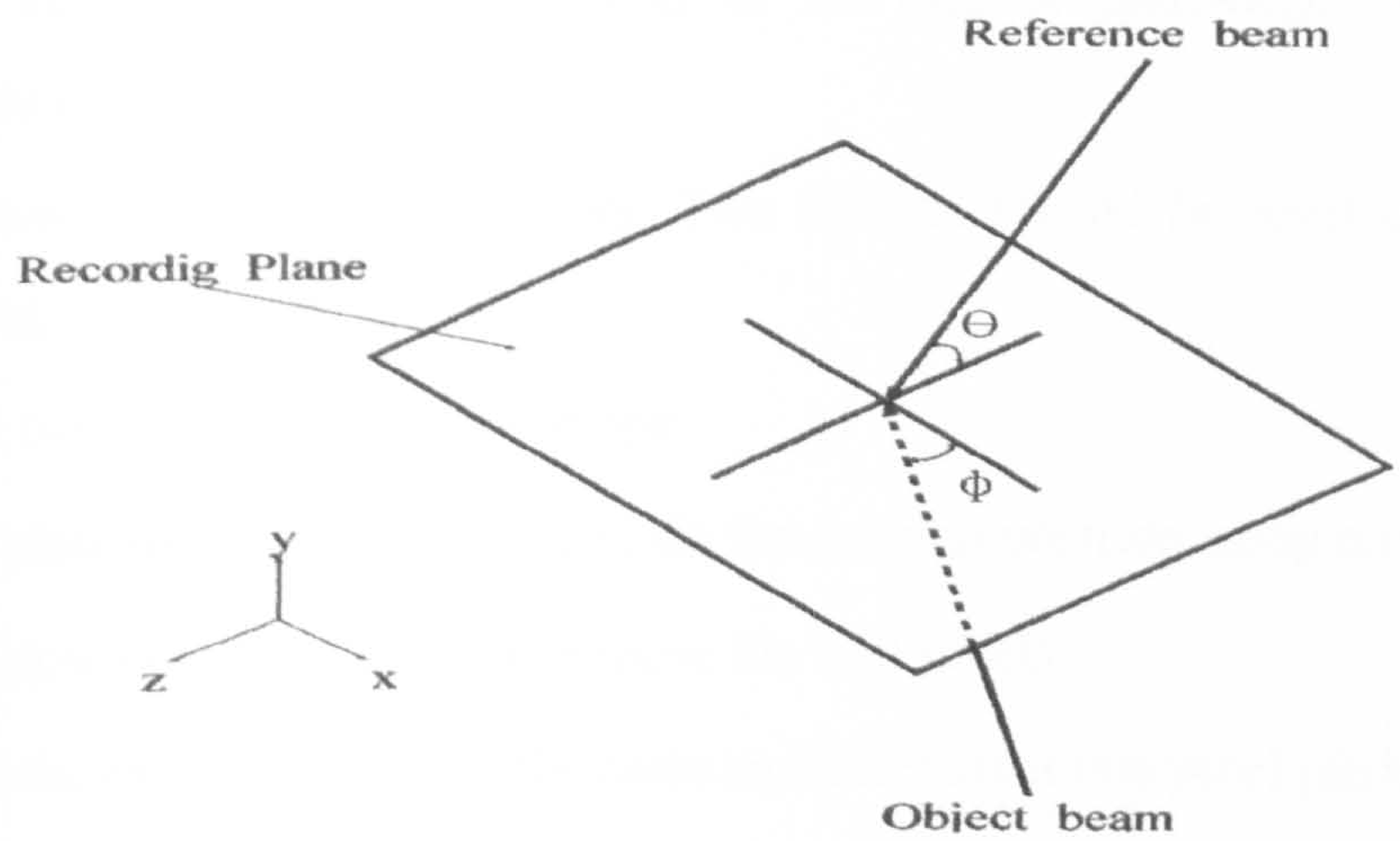


Fig. 7. 4 Recording geometry for 2nd and 3rd diffusers

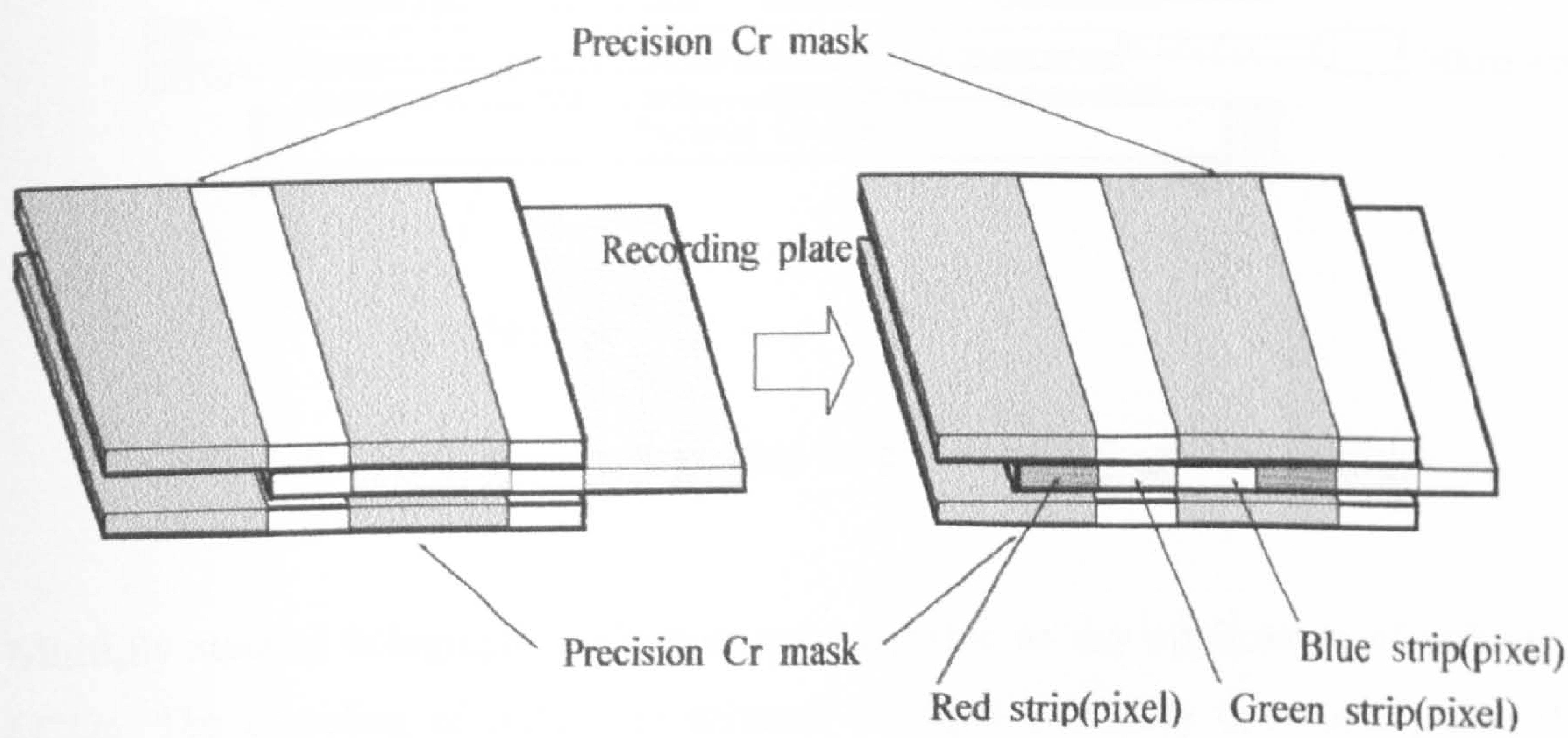


Fig. 7. 5 Schematic diagram for recording procedure and plate movement

To record pixellated HOE arrays, two identical masks have to be used. Unfortunately, it is very difficult to align to masks and to shift masks or plate precisely. Thus new apparatus for the recording of pixellated reflective HOE array has been designed, which is shown Fig. 7.6. Two identical masks are fixed on mask holders and move vertically to load the plate between them. The mask holders have fixtures with springs which press masks down to the plate to ensure that there are no gaps between plate and two masks. The plate is attached to a plate holder which can move horizontally. The movement of the plate is controlled by a micrometer at the end of plate-edge. The recording procedures are as follows:

1. Fix two masks to mask holders. Two holders should be leveled before plate loading.
2. Align two masks using microscope.
3. Load plate to the plate holder and fix the original position using micrometer.
4. Press down mask holders and expose the first pixels.
5. Move the masks away from the plate and translate it one pixel pitch.
6. Repeat steps 4 and 5 sequentially.

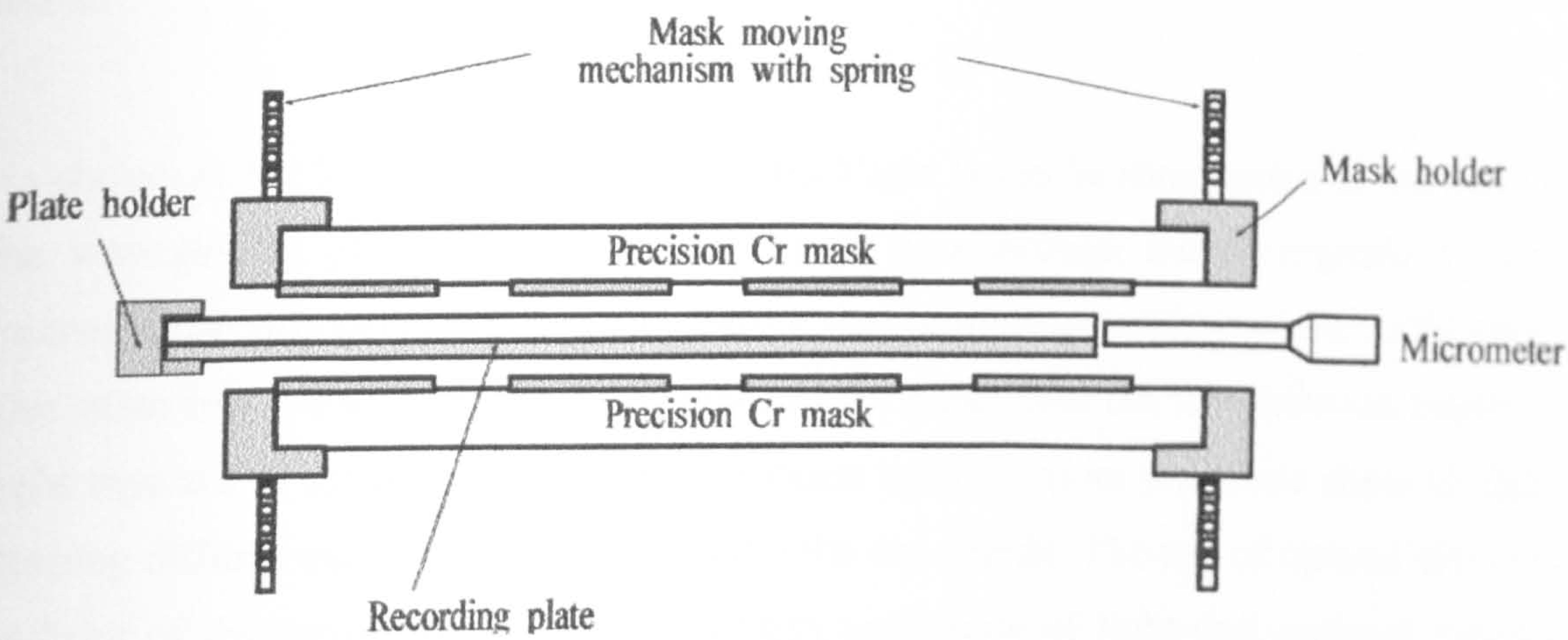


Fig. 7. 6 Mask aligning apparatus for pixellated holographic reflector

Multiply stacked holographic reflectors are adaptable to any application of reflective LCDs. The recycling of lights can enhance the light efficiency enormously and the degree of improvement may be more than 50%.

Although preliminary consideration and experiments have been done for development of multiply stacked holographic reflectors, it has not been finished. That is because this kind of development should be conducted in cooperation with the manufacturer of reflective LCDs to get the design of LCD pixel and to evaluate the devices in terms of display quality. Thus further researches will be executed shortly in cooperation with a company to make working holographic reflectors for the reflective LCDs and to investigate characteristics related to the colour representation and viewing angle.

7.3 LCD Backlight System using Extreme Angle HOE

7.3.1 HOEs for Backlight System

As outlined in paragraph 5.2.1, LCD backlights have been modified to accommodate the requirements of higher brightness, higher contrast ratio and wider viewing angle. Unfortunately however, there are limitations of improvement caused by their unusual shape.

As shown in Fig 5.1 and Fig 7.7, the LCD backlight has to be illuminated at the edge of the waveguiding plate. Some of the light rays pass through the waveguide by total internal reflection until they hit the scattering spot or transmitted toward the LCD panel. The other rays are directly transmitted toward the panel. But the transmission angles of light rays are so steep that several optical sheets such as micro prismatic sheet or light-shaping diffuser must be employed just after the waveguide. The use of optical elements in front of the waveguide is critical to obtain uniformity of light and optimal viewing angle. Thus if it is possible to adjust the transmission angle to be a right angle to the waveguide surface, the control of viewing angle would be more convenient.

In addition, the white reflector and the scattering dots that extract lights from waveguide can be substituted using new device employing the advantage of HOEs such as multifunctional characteristics and the capability of directing light to desired direction.

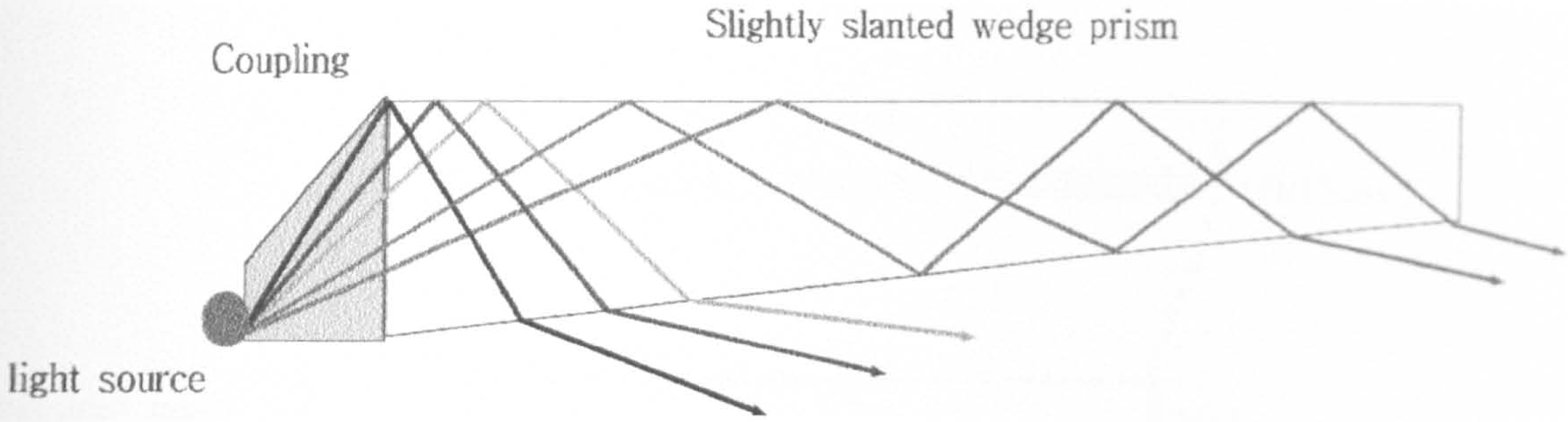


Fig. 7. 7 The ray diagram in the LCD backlight system

7.3.2 Extreme Angle Holographic Reflector

The optical arrangement for recording of reflective HOEs is just like the method described in section 6.3.2, which is shown in Fig. 7.8. The sheet beam shown in Fig. 6.3 illuminates the recording media through the edge of the optical flat lying underneath the recording media. The object beam incident upon the recording plate can be any type of coherent light, which is determined by the final use of HOE. For example, an optical element such as a diffuser can be used over the recording media. Normal collimated laser beam has been used as an object beam in this experiment just to diffract the incident light toward the upper direction.

For the replay of the HOE recorded with the method described previously, a waveguiding plate such as a wedge prism or optical flat should be attached to the reverse of the HOE. If we use a holographic AgHal emulsion coated on a glass substrate (thickness ≈ 2.6mm), the gap between waveguiding plate and holographic emulsion may be too big. Thus holographic AgHal film (thickness ≈ 250μm) manufactured by Slavich [7.10] has been used and an optical flat made out of optical glass which has the refractive index of 1.52 was employed as a waveguiding plate (t ≈ 5mm). The holographic AgHal film was laminated onto the waveguiding plate using UV curable epoxy bond. The reflectance was measured using spectrophotometer described in Chapter 2. The reflectance of typical samples recorded with the wavelength of 532 nm at an angle of 85° was about 80%., which are illustrated in. Fig. 7.9.

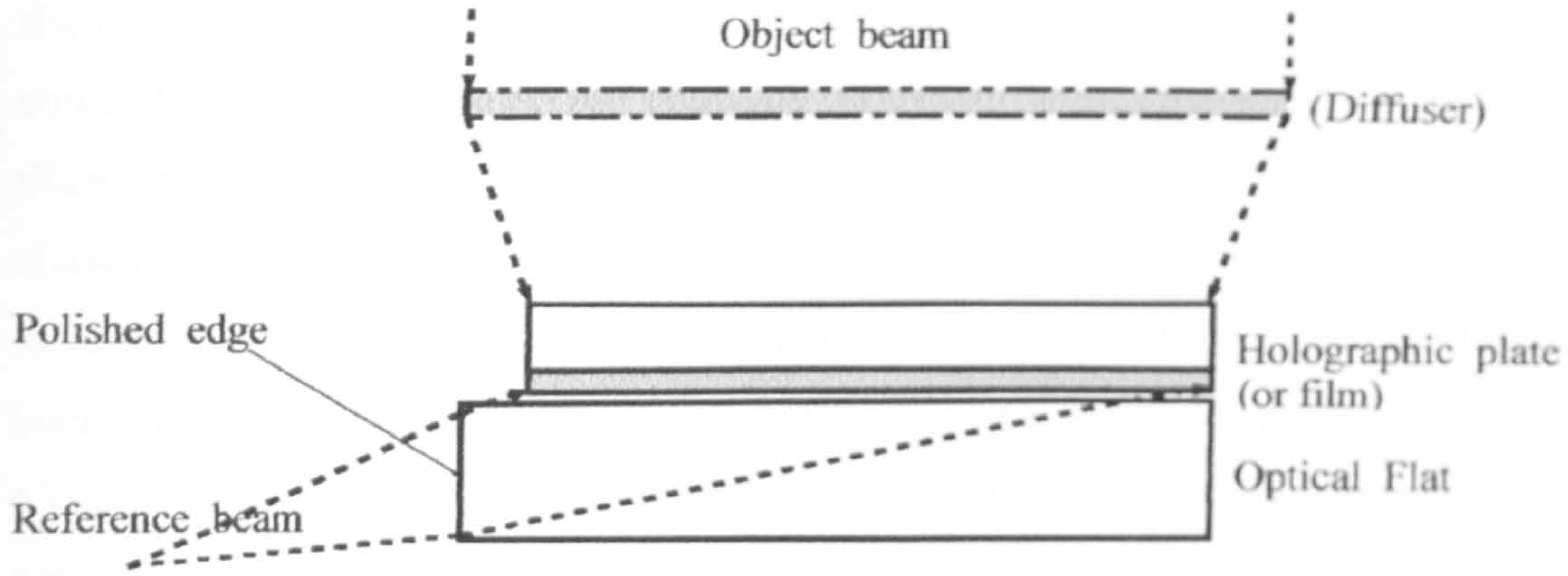


Fig. 7. 8 Optical arrangement for recording extreme angle reflector

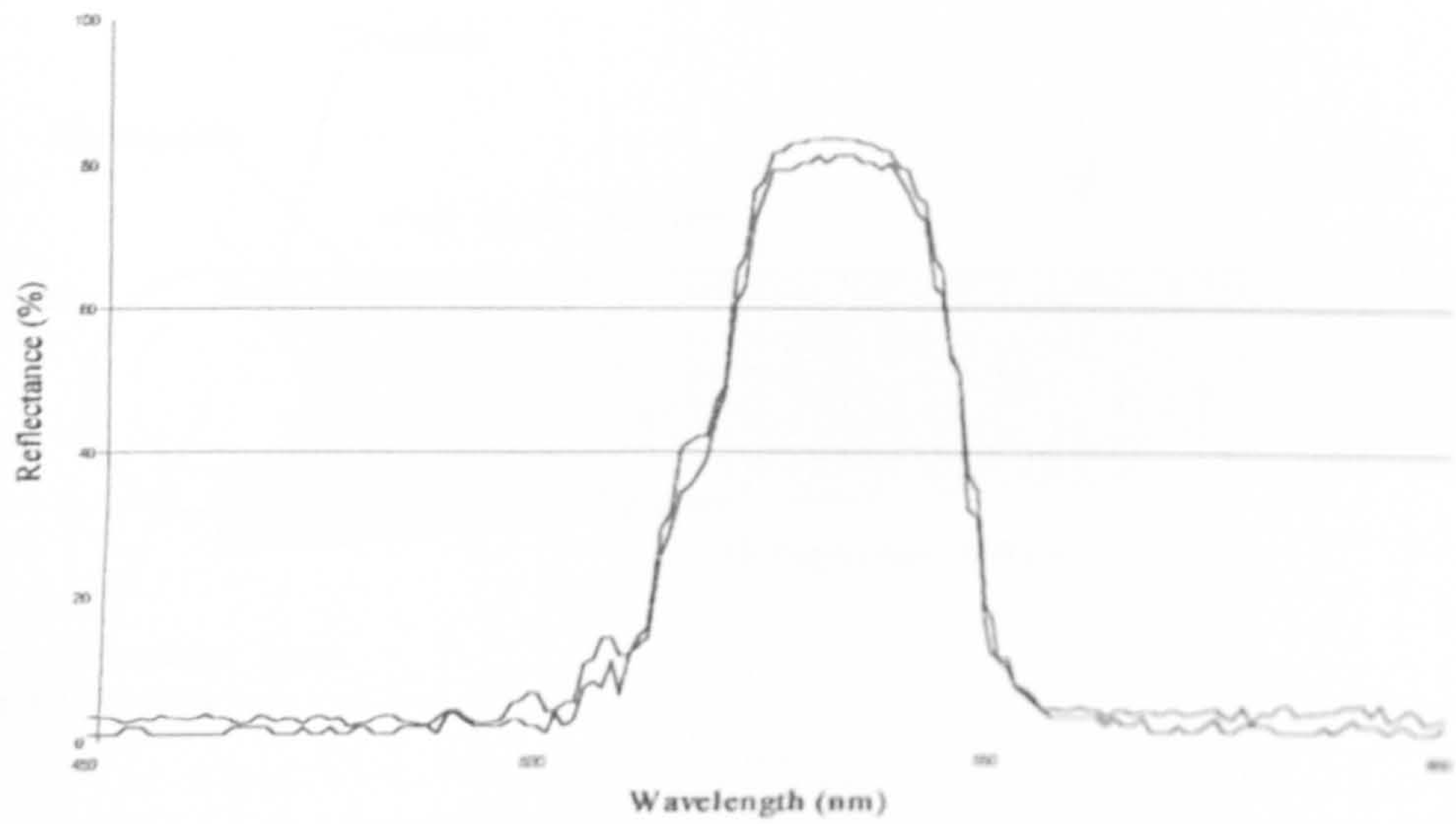


Fig. 7. 9 Reflectance of two HOEs recorded at an extreme angle (85°)

7.3.3 Backlight Design and Preliminary Test

A simple structure of backlight has been designed using reflectors described in last section. The structure of the backlight illustrated in Fig. 7.10 consists of light source with reflector, waveguide, coupling, holographic reflectors and wide-angle diffuser. The roles of each component are as follows: Both CCFLs (cold cathode fluorescent lamps) and LEDs (light emitting diodes) could be employed as a light source of which the spectrum is adjusted to match that of LCD colour filter. If a holographic reflector has been used in the optical system as a backlight, the use of a coupling structure enhances the efficiency of light in the system because the profile of light or wave front can be controlled by the shape of the coupling structure. It is also good for the uniform illumination of holographic reflectors. Holographic reflectors consist of double or triple-stacked reflectors that diffract red, green and blue or blue and yellow light respectively toward the direction of LCD panel. Waveguide is an ordinary one used in LCD backlight but there is engraved portion at the edge, which act as coupling structure. The diffuser used on the top of the backlight scatters the light from the waveguide widely. It may be useful to employ high reflective coating at the reverse of the holographic reflector to reflect transmitted light.

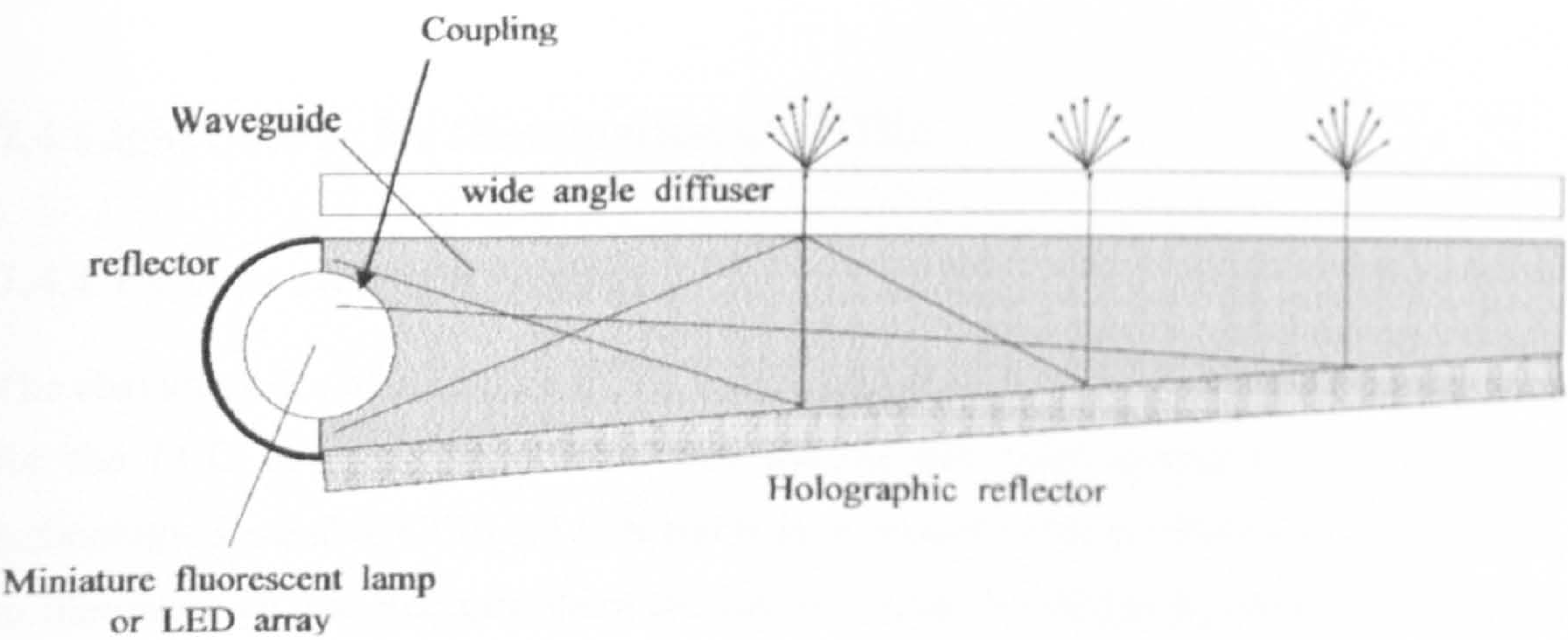


Fig. 7. 10 Schematic diagram of a backlight with holographic reflector

A holographic reflector, which has the size of 5 inches diagonal, has been recorded with Nd-YAG laser (λ = 532nm) at the angle of 85° and laminated onto a wedge prism. Then a green LED array (4 LEDs) was employed at the edge of the wedge prism and a wide-angle diffuser was attached on the waveguide. The application of LED array will be discussed in the next section. The result of preliminary test for the monochromatic backlight is shown in Fig. 7. 11. Using this backlight mentioned above makes it possible to enhance the brightness as well as viewing angle of LCD panel and the structure will be simpler than that of conventional backlight system.

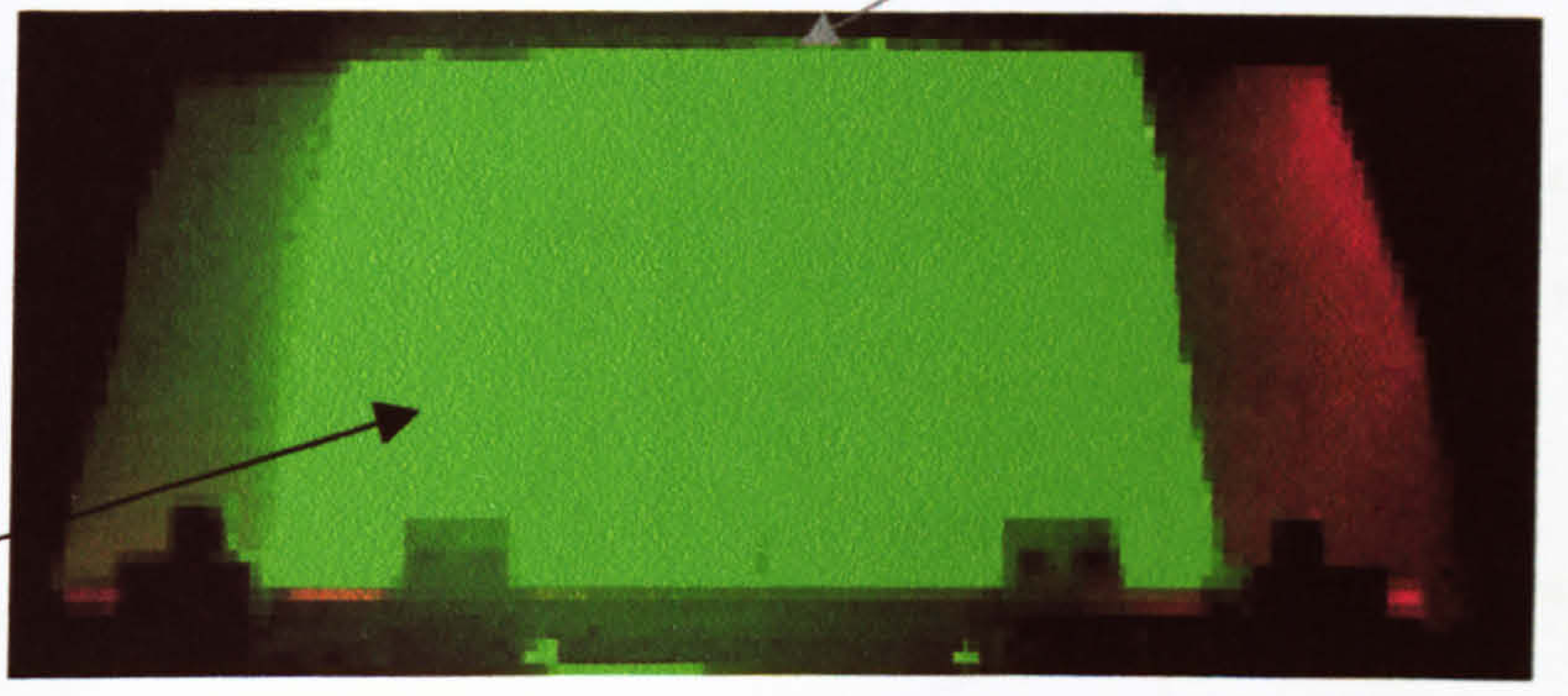


Fig. 7. 11 Illumination test of backlight

7.4 Light Source for Illumination of HOEs

7.4.1 LED as an Light Source

The characteristics of miniature CCFL (cold cathode fluorescent lamp) as a light source for the LCD backlight have been well known and used extensively in the LCD technology. Instead of CCFLs, LEDs has been investigated as an alternative light source to illuminate HOEs. Recently there are lots of LEDs developed by several companies such as Nichia Corporation, LumiLeds Lighting [7.11] (Agilent's joint-venture partner with Philips Lighting), OSRAM Opto Semiconductors, Stanley Electric, Matsushita Electric Co., Sharp, and Citizen Electronics. The characteristics of brightness and colour representation are improving dramatically.

The most remarkable results have been achieved by a company called LumiLeds Lighting. LumiLeds Lighting has introduced several white and colour LEDs, which are the brightest LEDs ever developed. CIE colour chromatography of those LEDs has been obtained using colourimeter illustrated in Fig. 7.12, which shows that the white balance is almost perfect in terms of the display system. The spectrum of white LED is shown in Fig. 7.13. Because white LED is made from blue LED coated by yellow phosphor, there are two peaks at the blue and yellow wavelengths.

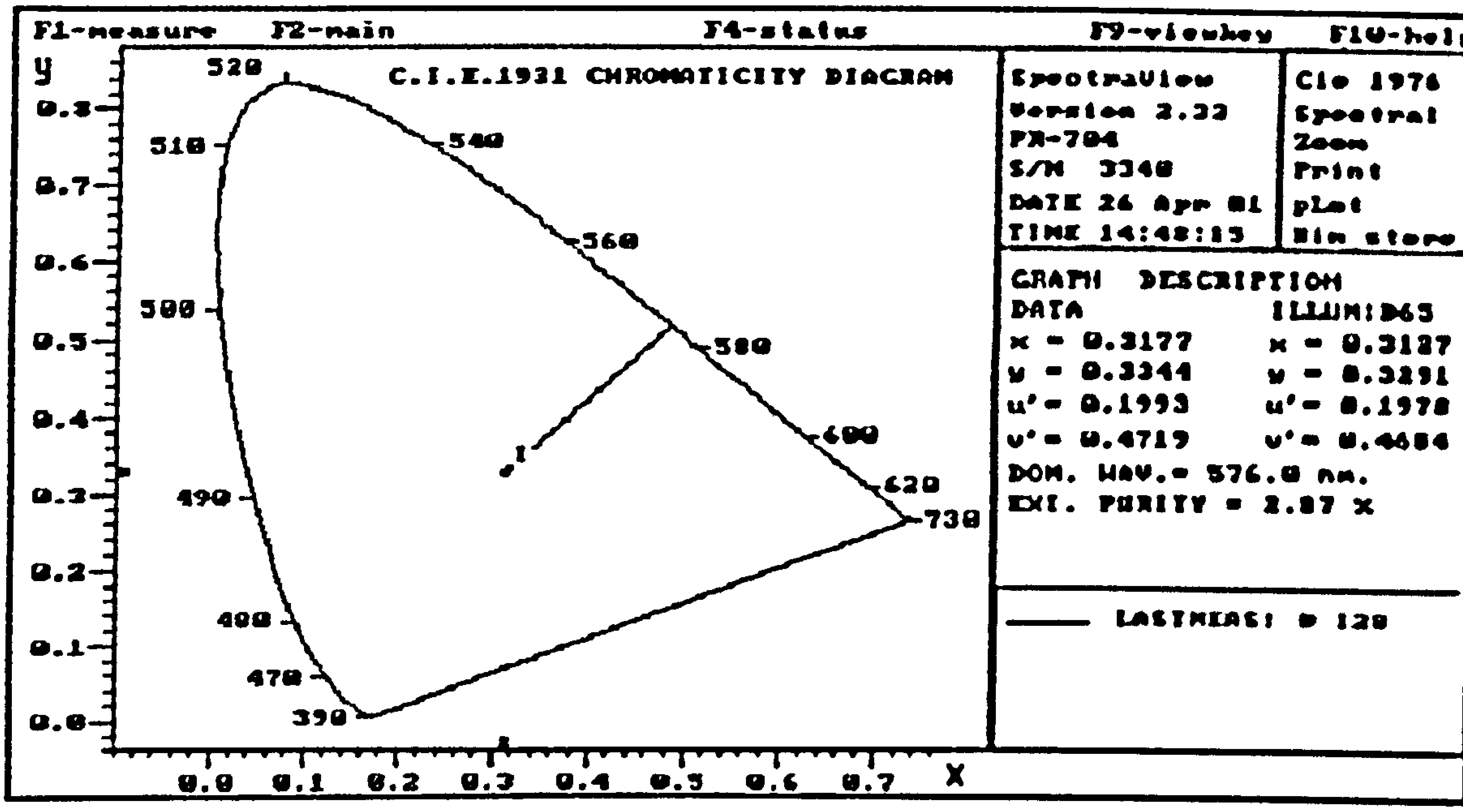


Fig. 7. 12 CIE chromacity diagram of withe LED produced by LumiLeds Lighting

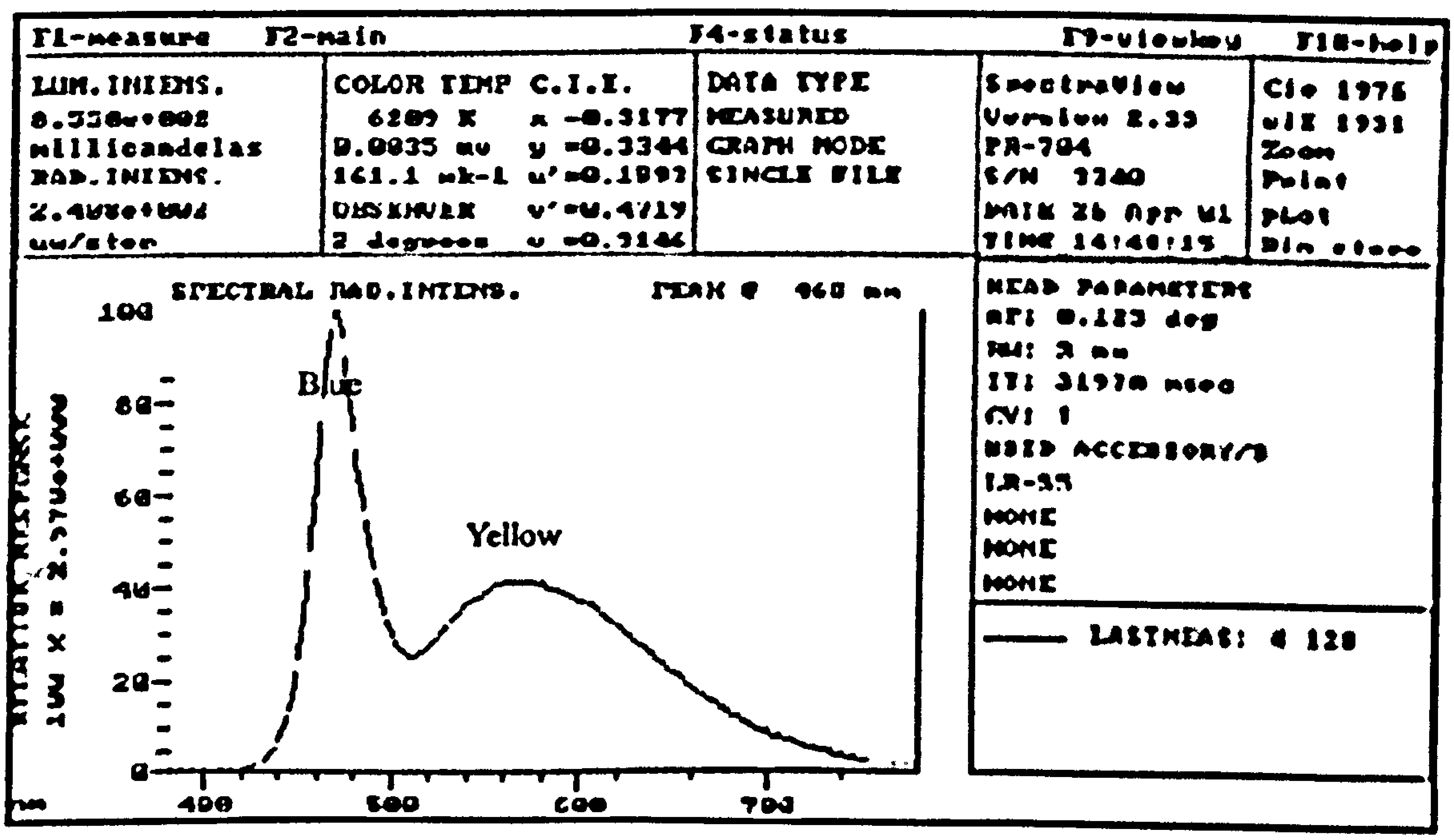


Fig. 7. 13 Spectrum of white LED produced by LumiLeds Lighting

7.4.2 Illumination Test Using LEDs

If an LED is used in an optical system independently, the brightness of each LED is still too low to be applied to an illumination system. Thus the application of LED arrays is considered for the illuminating light source. As LED itself has considerable size and LED arrays acts as a multiple light source, there are dark gaps on the illuminated zone and diffracted image produced by illuminating HOE may be blurred. Thus the beam produced by LED arrays should be homogenized in any case.

The profile of the beam emitted from white LED arrays has been evaluated using the optical arrangements shown in Fig. 7.14 and Fig. 7.15. The size of lens was 25 mm in diameter and the focal length 45 mm. White LED from LumiLeds Lighting has been used as a light source and convex lenses are employed to collimate the light beam. The measurements have been performed by projecting the beams onto a screen and evaluated using a beam profiler. The distance between collimating lens and screen was varied from 10 cm to 150 cm to find the optimal distance and obtain uniform profile.

As shown in series of data shown in Fig. 7.16, it appears that there was some colour dispersion and the beam divergence was about 0.4° measured at 1 m in terms of FWHM (full width at half maximum). As the distance became longer, the nonuniformity at the boundary got homogeneous and the distance should be at least 1 meter to obtain uniform light beam. Unfortunately however 1 meter is so long for the practical optical system that another optical element should be necessary in front of LEDs to minimize the distance between LEDs and illumination points. A light shaping diffuser has been used in front of LED array to homogenize beans from LED arrays. The scattering angle of the beam shaping diffuser was 0° in vertical direction and 10° in horizontal direction. Using beam-shaping diffuser in front of LED arrays, the distance of uniform illumination has been reduced to 20 cm.

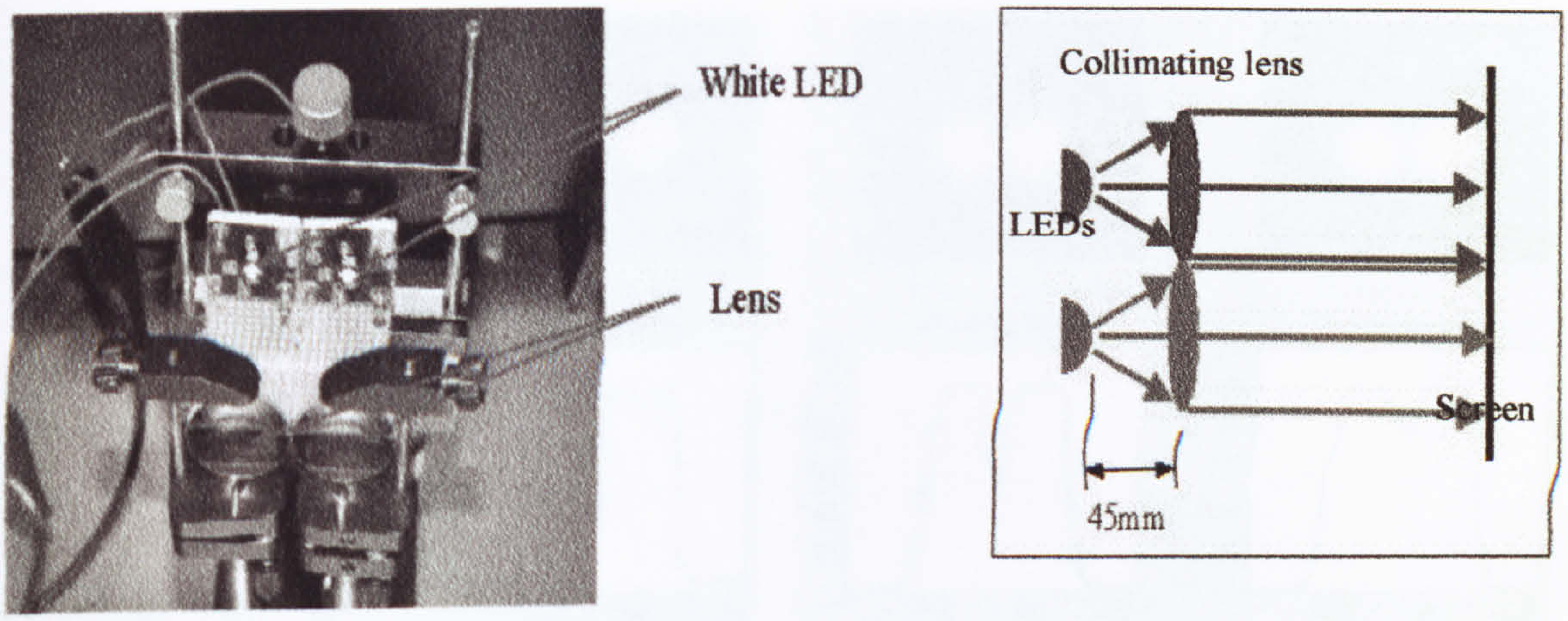


Fig. 7. 14 Beam profile measurement setup for LED arrays

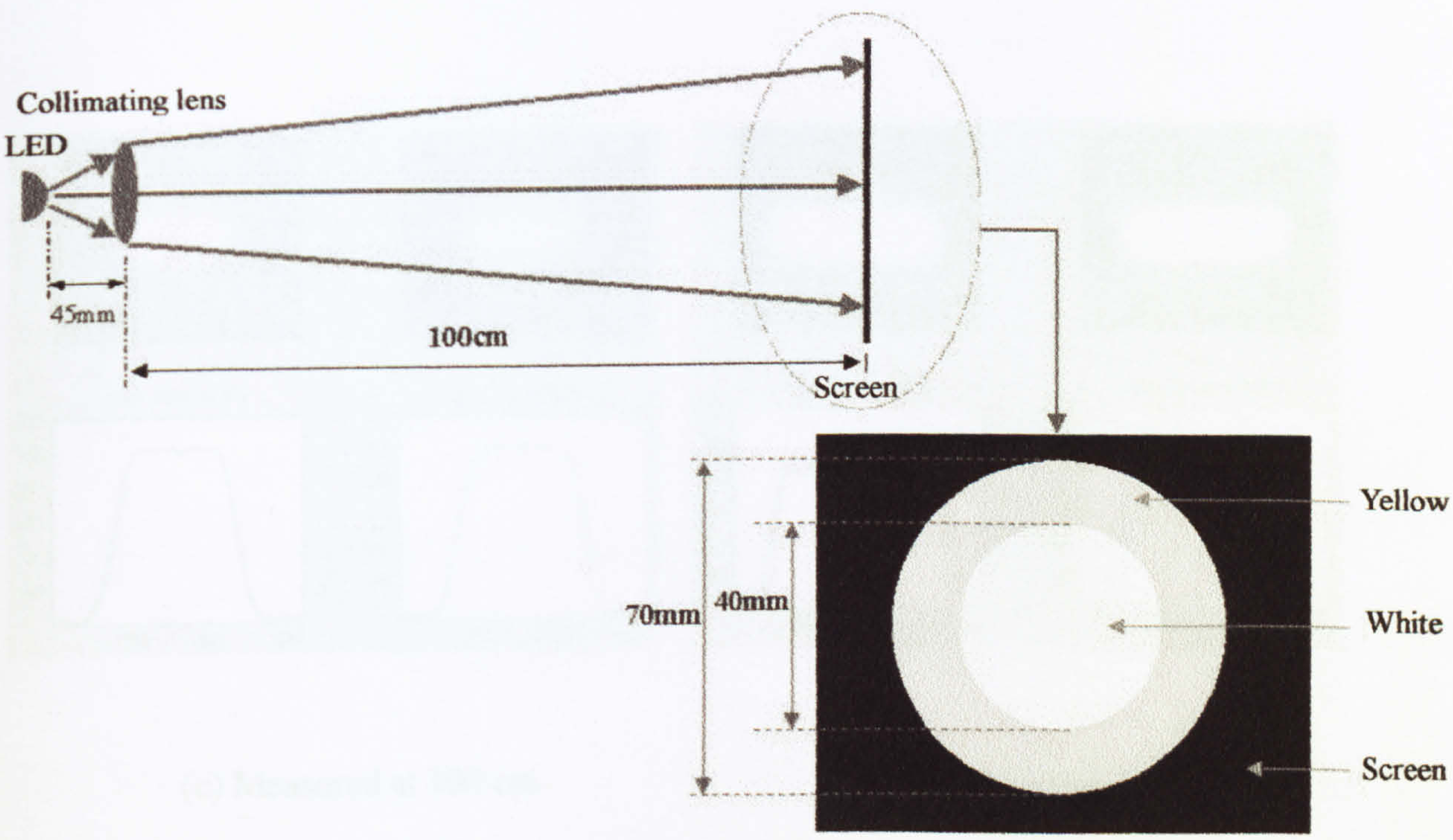
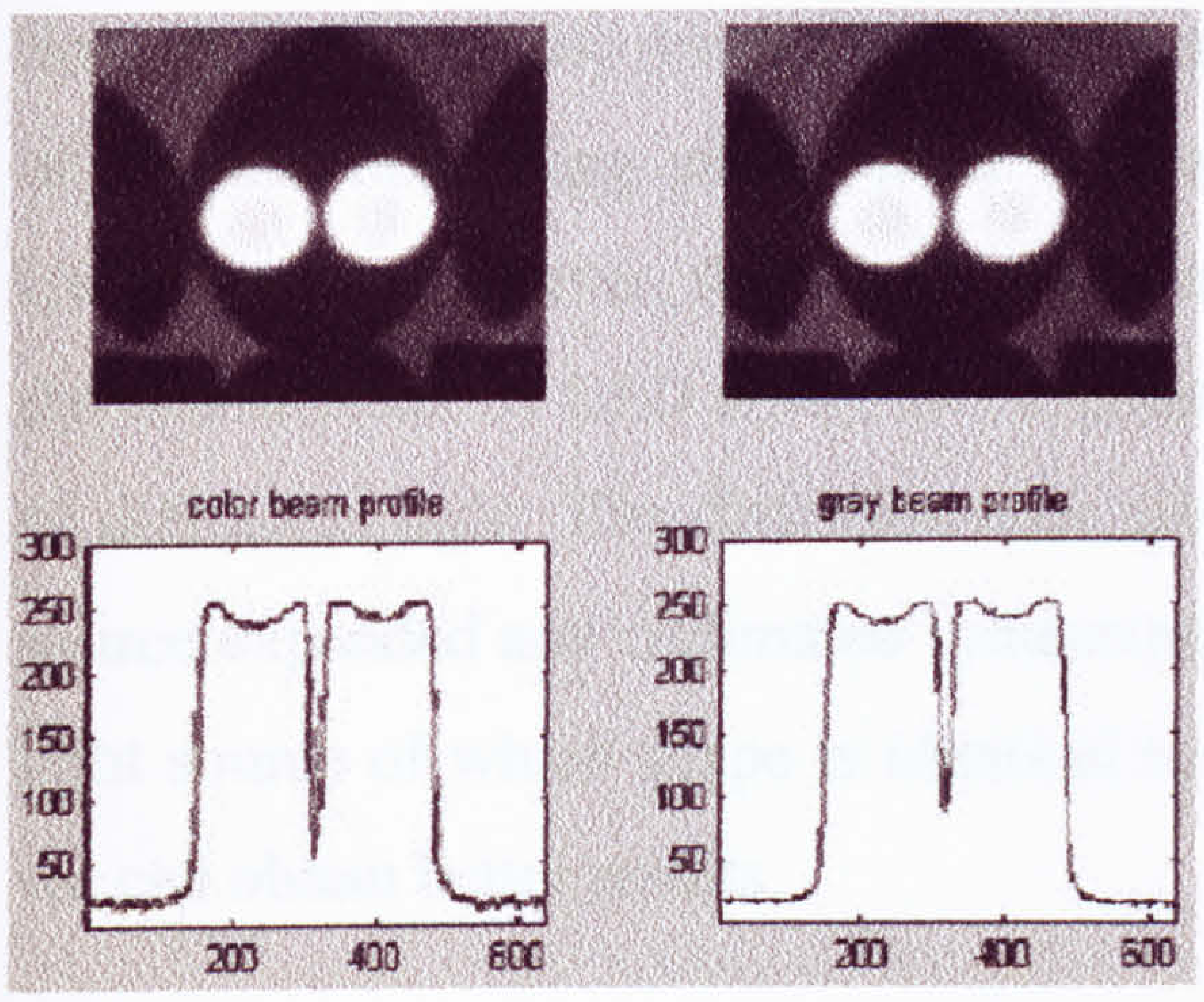
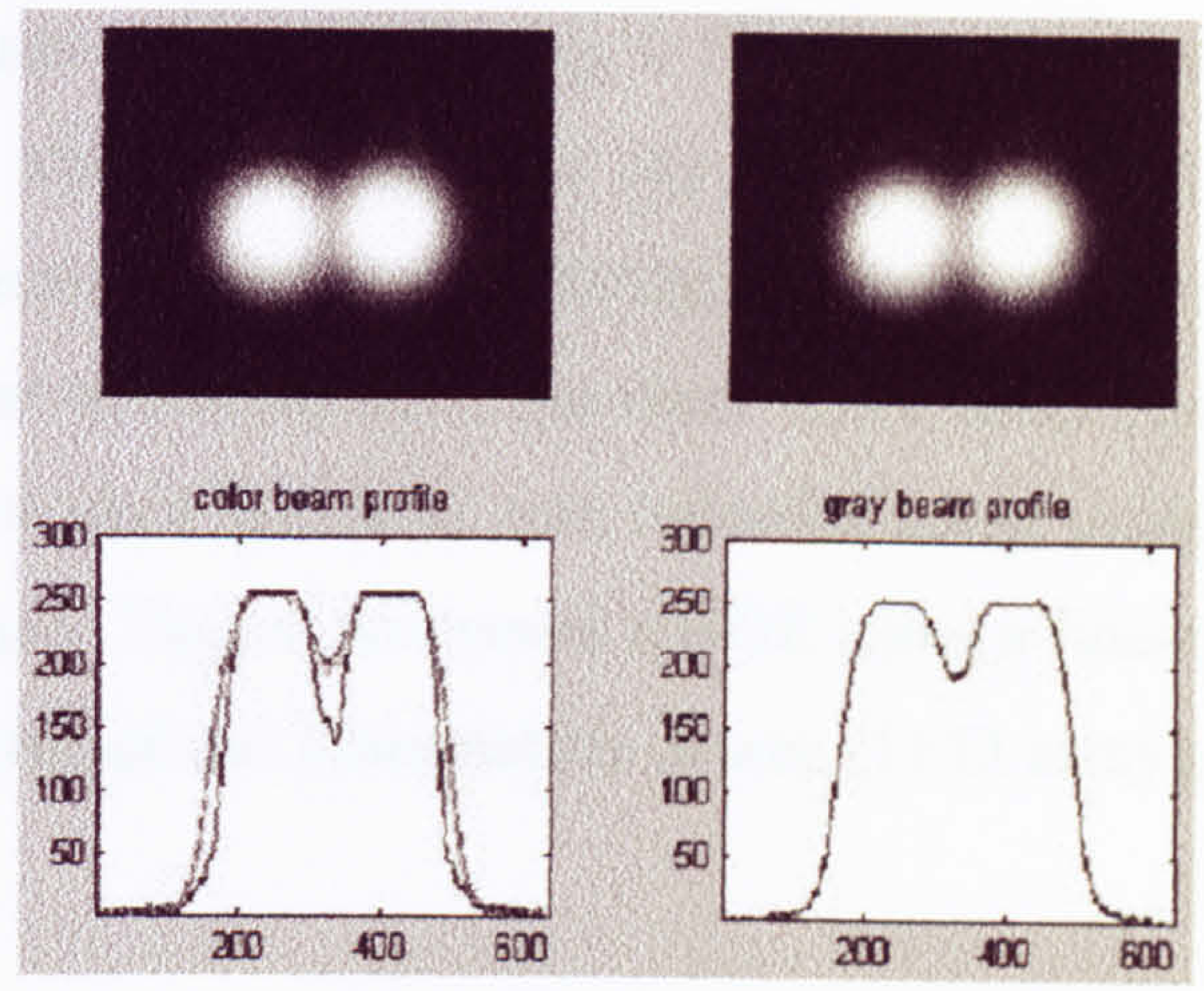


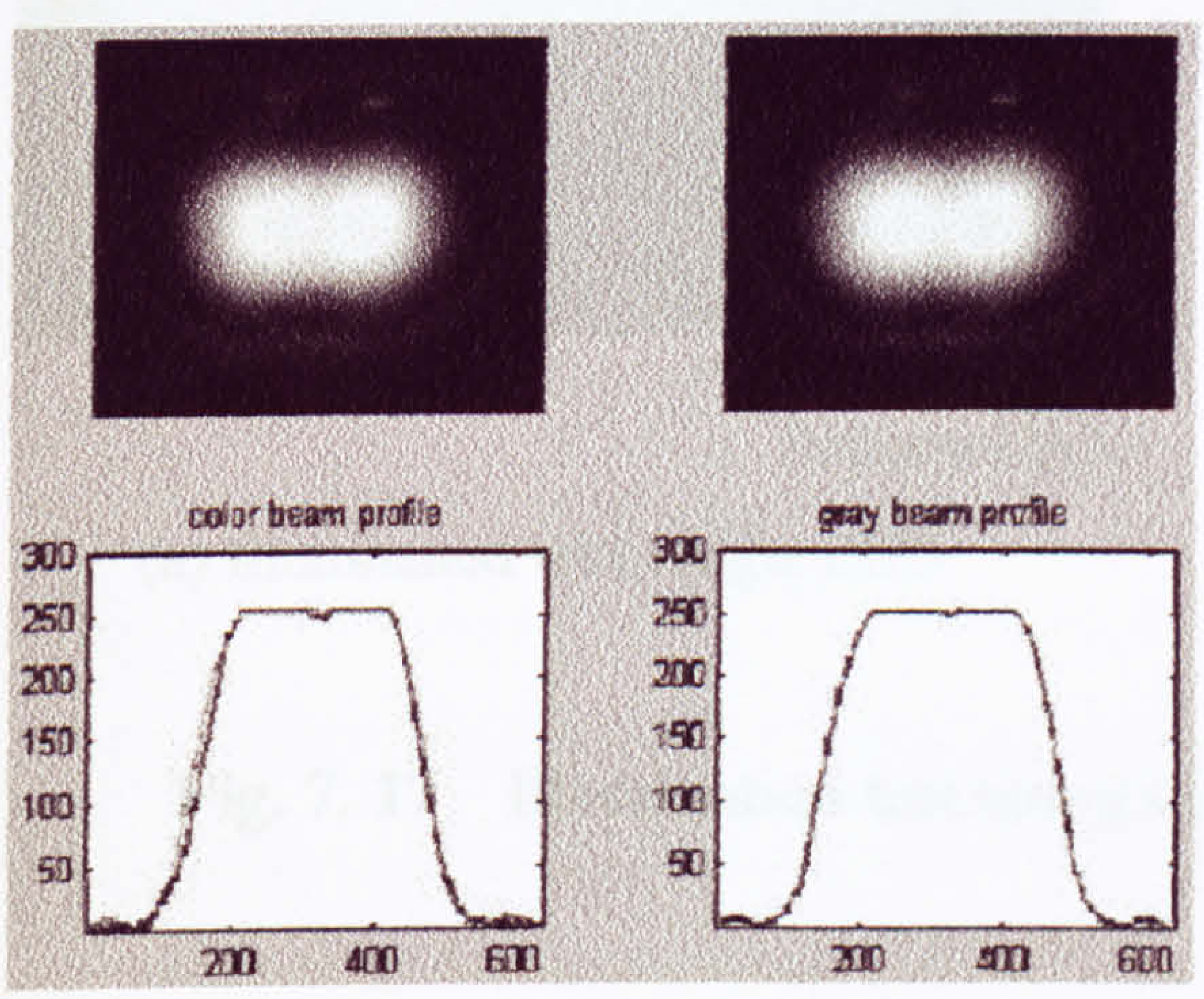
Fig. 7. 15 Beam profile of white LED measured at a screen aparted 1 meter from light source



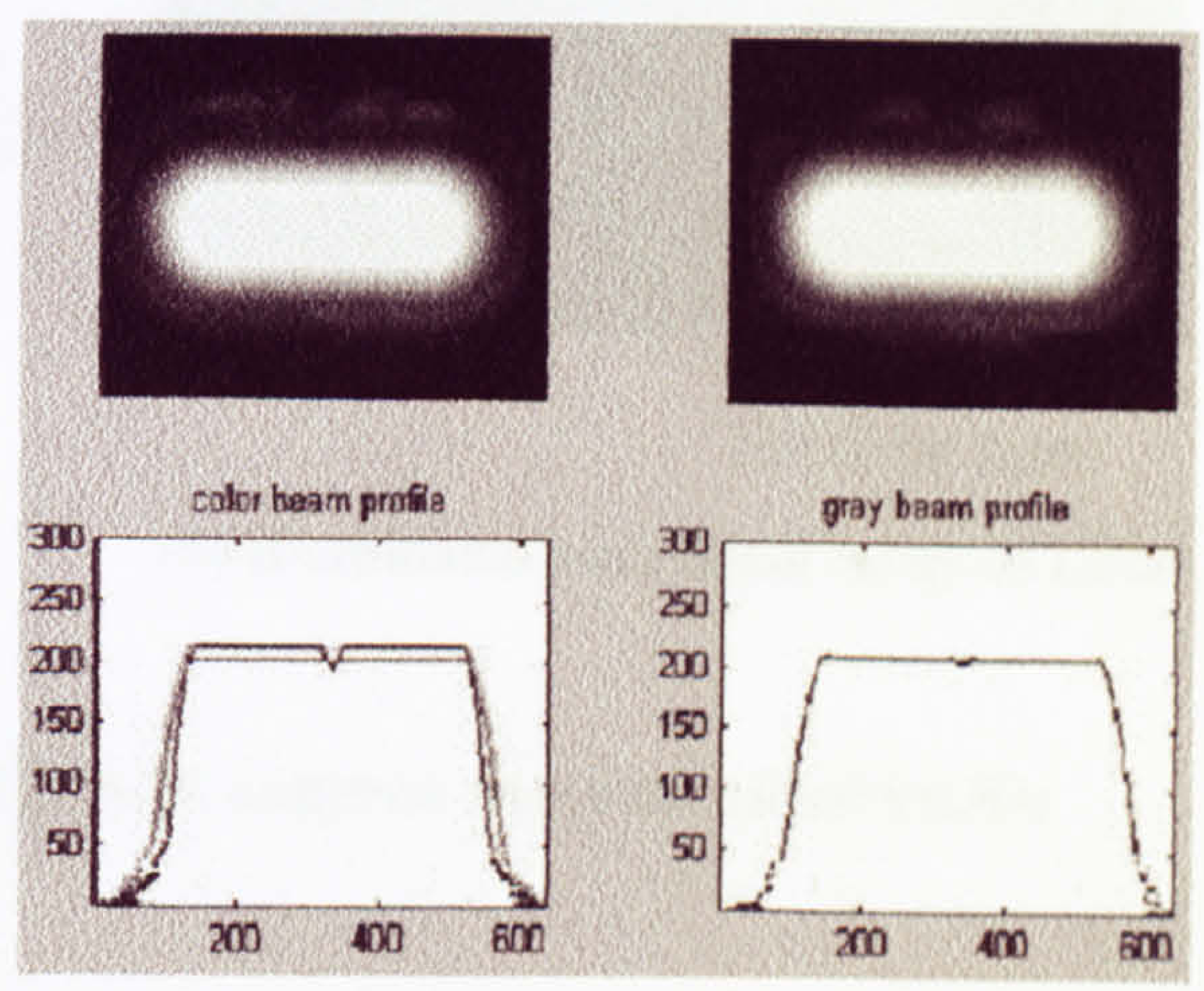
(a) Measured at 10 cm



(b) Measured at 50 cm



(c) Measured at 100 cm

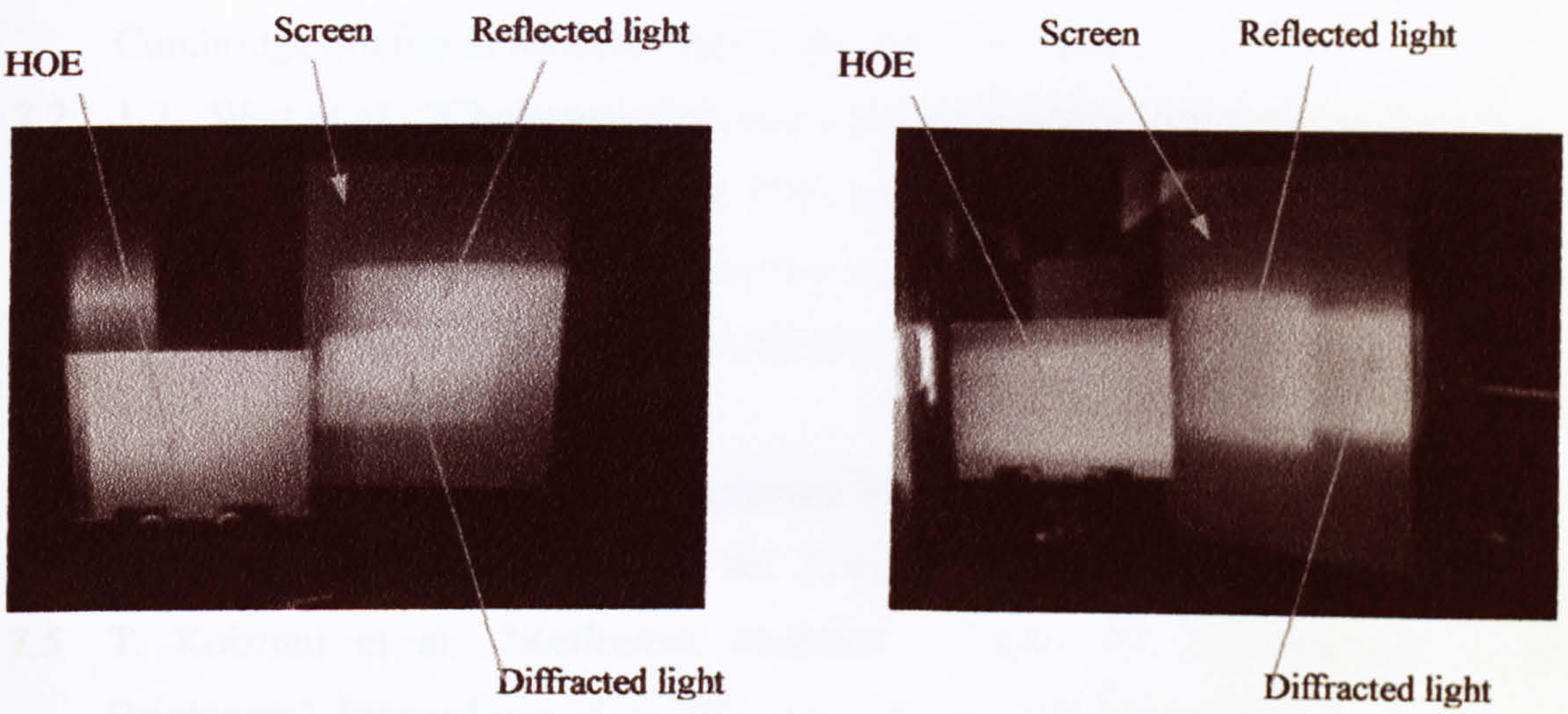


(d) Measured at 20 cm

(with beam shaping diffuser)

Fig. 7. 16 Measured beam profile of LED light source

The illuminating test has been tested using holographic reflector and a green LED or linear array (4 LEDs) respectively. The results can be seen in Fig, 7.17. The uniformity of illumination using single LED source shown in Fig. 7.17 (a) was quite good. Unfortunately however, the illumination was not bright enough for the practical use. For the illumination by LED array, the brightness was acceptable, but there was a distortion of diffracted light. The distortion took place since the HOE was recorded using point source expanded and collimated symmetrically. Thus if we record a HOE using a linear light source of which shape is identical to that of the illumination source (LED array), we can obtain better results.



(a) Illuminated with single LED

(b) Illuminated with linear array of LEDs

Fig. 7. 17 Illumination test using LEDs with extreme angle recorded HOEs

7.5 Conclusion

Various applications of SHSG processing method have been examined to demonstrate the feasibility of the SHSG processing. Several HOEs, which can be used for improving the quality of display systems, have been developed. Successful results are derived from several investigations such as holographic diffuser, holographic reflector and HOEs recorded at extreme angle

The possibility of making newly designed optical devices using SHSG process has been investigated. Multiply stacked holographic reflector has been designed for the application to reflective LCDs and new simple structure of LCD backlight with holographic reflector and diffuser has been proposed to improve light efficiency as well as viewing angle.

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Chapter 8

Manufacturing of SHSG-processed HOEs

8.1 Apparatus for Recording HOEs

8.1.1 Optical Setup with Vertical Arrangement

Generally, optical components for holographic recording are arranged on the optical table horizontally. In this case, as the size of the recording plate increases, the arrangement becomes more complicated because it is very difficult to align laser beams and to hold the recording plate without vibration. Thus a vertically arranged optical setup is inevitable for large-scale holographic recording. For this kind of arrangement, optical components should be mounted very firmly and the optical setup should be robust enough to avoid any vibration during the recording. Therefore new designs for a vertically arranged optical setup have been considered in this work.

For the purpose, mentioned above, a mount for large optics such as collimating lenses and mirrors was constructed on the optical table. This construction is made from very thick (15~20 mm) black-anodized aluminum plate which doesn't reflect light and scatter light randomly. There are lots of holes and slots in the walls to mount optical components, which are as big as 600 mm × 800 mm.

This construction is an enclosed system and has a lid and opening doors to ensure that any turbulence of air is prevented. There are only two openings, for the reference and object beams. The size of opening is adjustable according to the beam size by using plates of various sizes. Using this construction in the recording of HOEs, the optical arrangement is very flexible and the stability of the optics is remarkable. In this work, many HOEs larger than 300 mm × 400 mm, have been recorded using this construction. Examples of optical arrangement are shown in Fig.8.1 and a drawing of the newly designed optical construction is illustrated in Fig. 8.2

Fig. 8. 1 Exmaple of vetically arranged optical setup

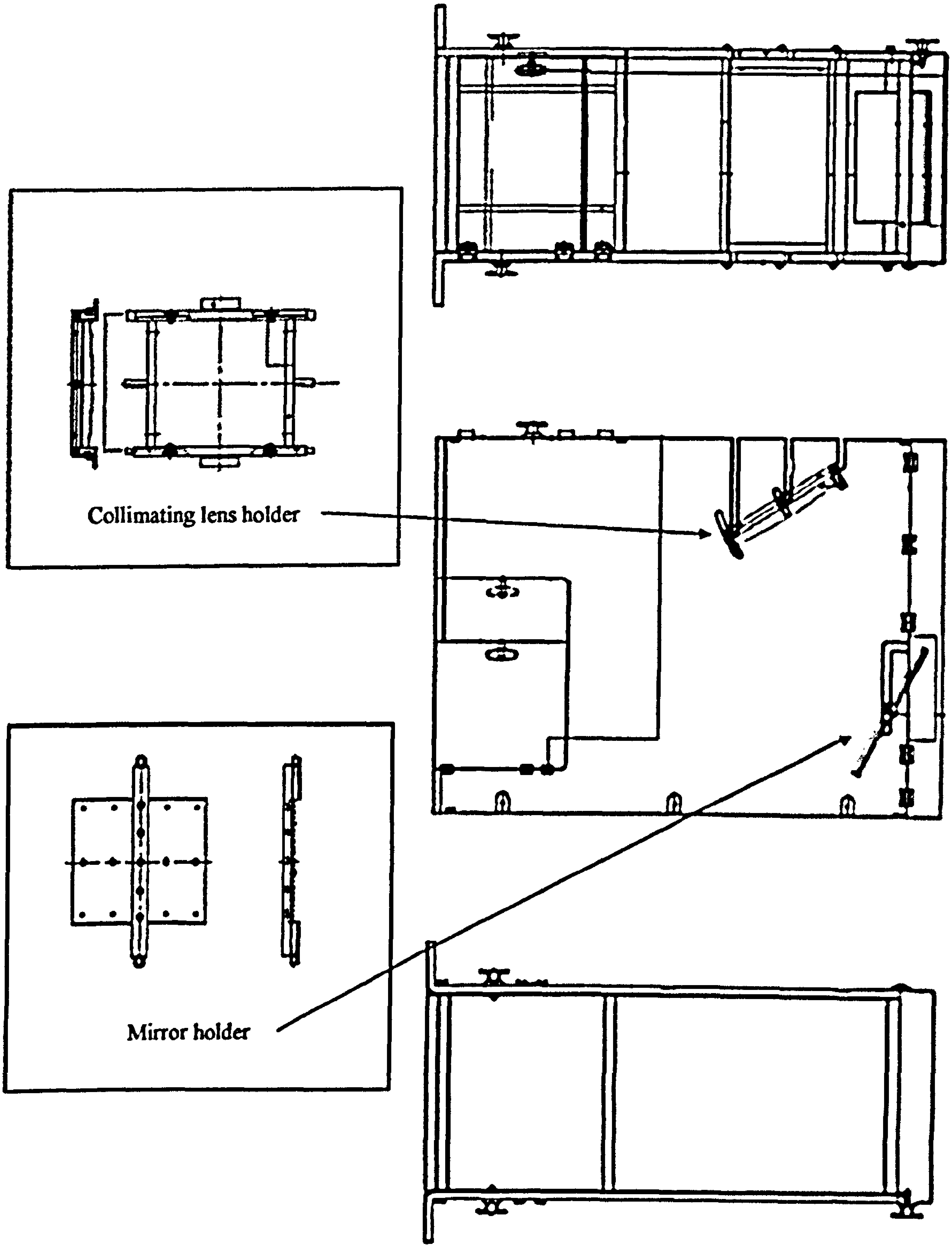


Fig. 8. 2 Drawing of construction for vertically arranged optical setup

8.1.2 Mask Aligner

To record HOEs with micro-sized patterns, a precision mask has to be used to form patterns in the recording materials. If there are two or more patterns to be recorded, the mask should be possible to move precisely according to the pattern size. When a mask is used in the holographic recording, index matching is necessary to avoid the occurrence of unwanted interference fringes. It is very difficult to move mask precisely in the presence of index matching fluid. A mask aligner has been designed and fabricated to solve these problems as shown in Fig.8.3. The mask aligner consists of various mechanisms such as an index matching fluid tank, micrometers to measure the mask movement, a plate holder, clips to fasten the plate, pins for positioning the plate and a hanger for mounting the mask aligner in the setup. A practical model of this design is illustrated in Fig. 8.4.

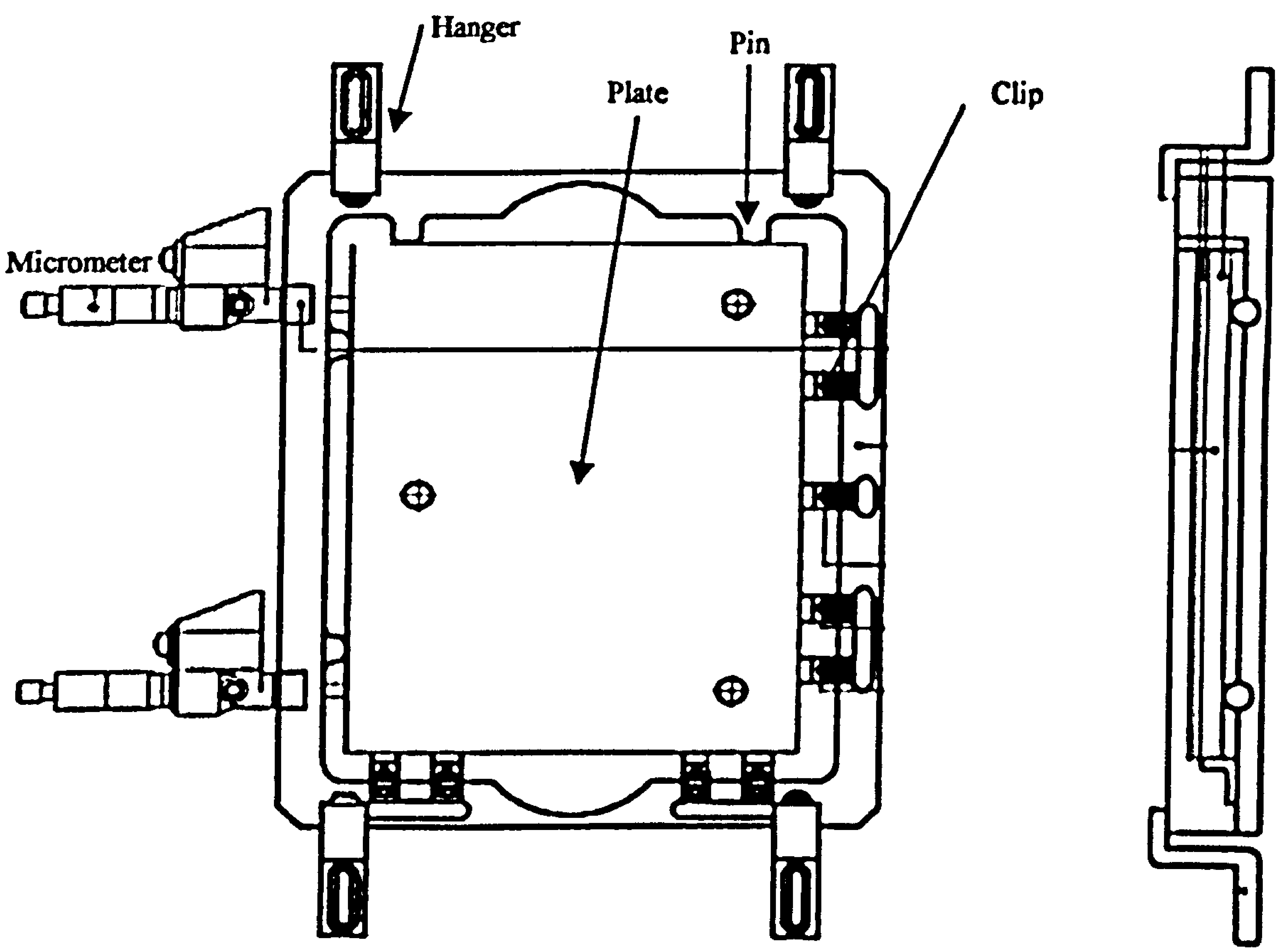


Fig. 8. 3 Drawing of mask aligning tank

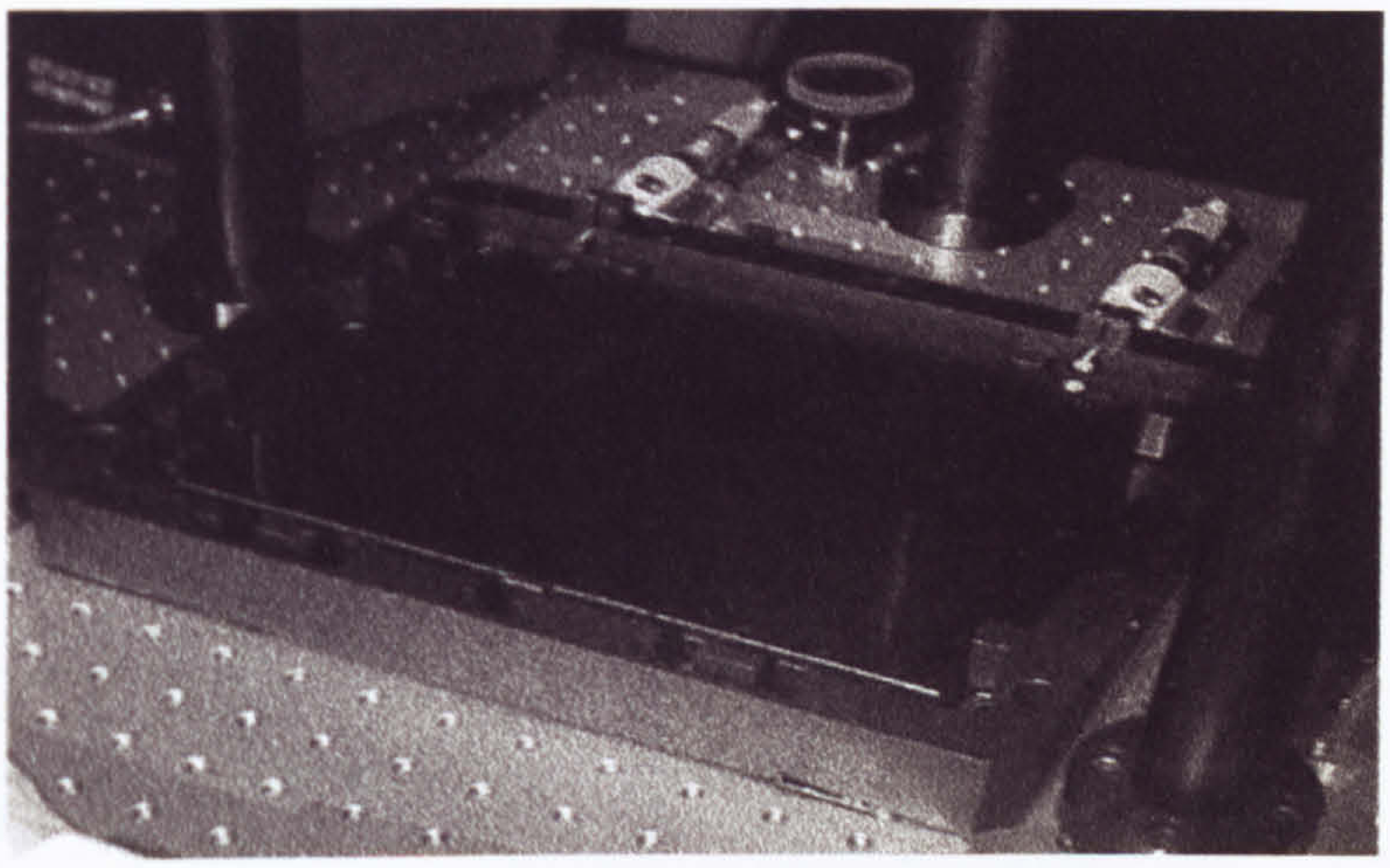


Fig. 8. 4 Practical model of mask aligning tank

8.1.3 Symmetrically Beam Splitting Device

In the holographic recording process the source beam need to be split into two beams, reference and object beam, which are mutually coherent. A polarizing beam splitter is often used for this purpose. The coherence length of the laser beam is very important to obtain maximum interference. Thus the optical path length from the origin to the target (recording media) should be nearly equal for both the reference and the object beam. Normally, it is very hard to adjust the optical path length since the polarizing beam splitter splits the beam into to parts, which differ from each other 90° both in polarization and direction. An apparatus has been designed to split the beam into two equally polarized parts. Fig. 8.5 is a schematic drawing of the apparatus and Fig. 8.6 illustrate how it works. The working principle and functions of each component are as follows

- a ⊙ polarized beam is created by the input beam component,
- a ↔ polarized beam is produced by input beam component,
- The ↔ polarized light passes twice through the λ /4 wave plate (retarder) and become a ⊙ polarized beam before reflection,
- The λ /2 wave plate (retarder) determines relative magnitude of ⊙ and ↔ polarization of the input beam.

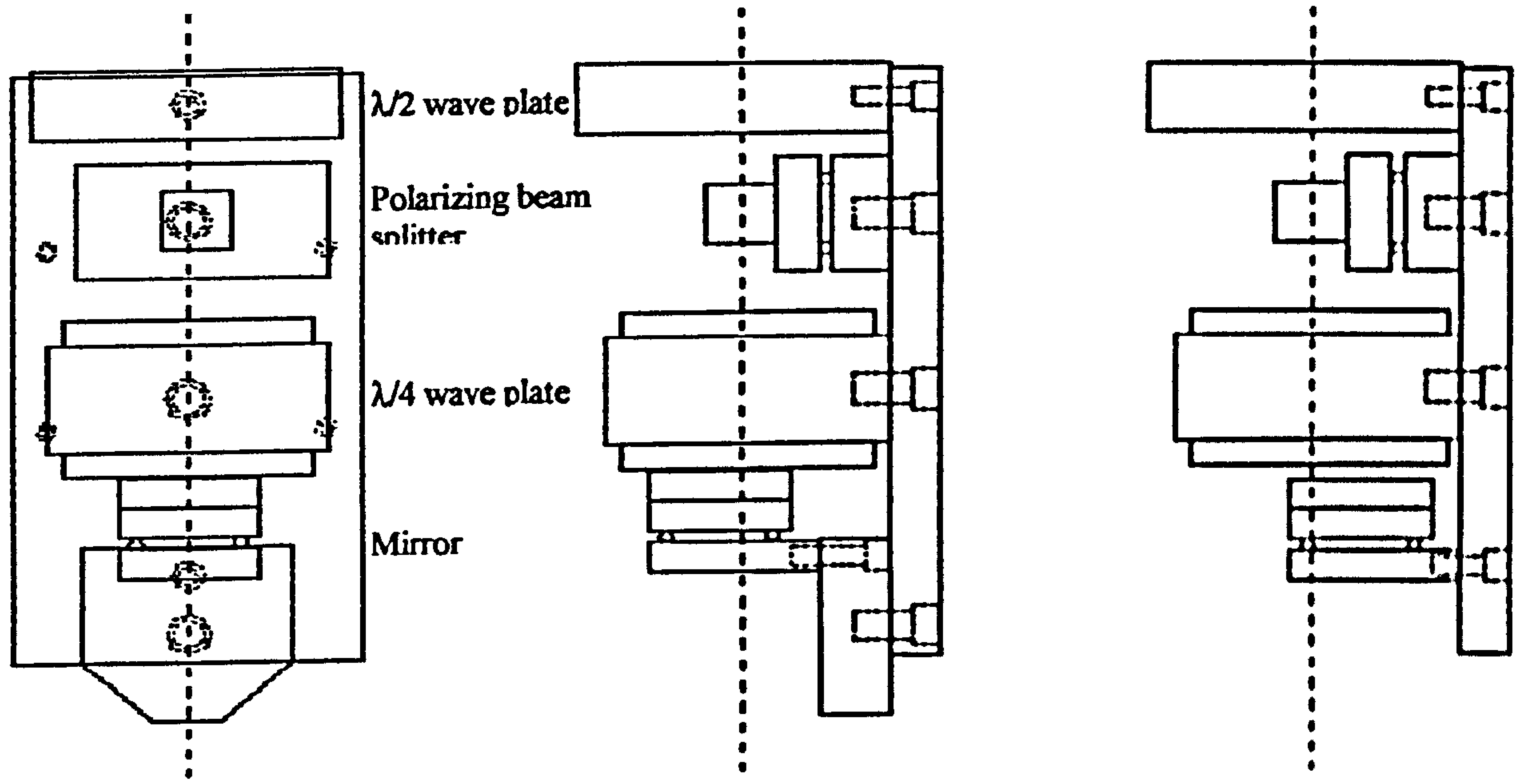


Fig. 8. 5 Schematic drawing of symmetrically beam splitting device

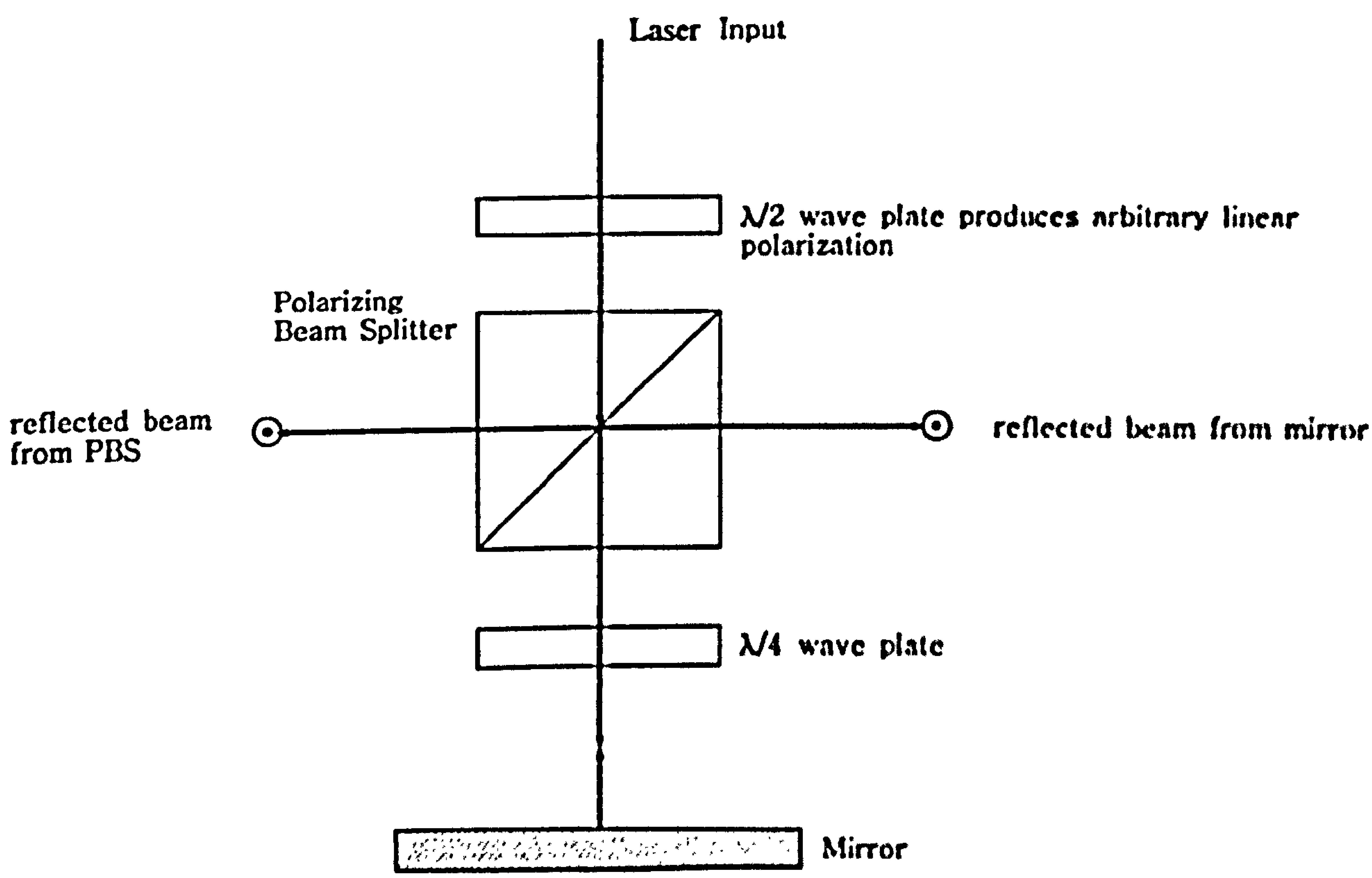


Fig. 8. 6 Operating principle of symmetrical beam splitting device

Fig. 8.7, 8.8 shows an example of optical arrangement to make a transmission grating recorded at an angle. Both reference and object beam are symmetrically arranged, that is the polarizations and optical paths of two beams are nearly same. This apparatus is very useful for recording a fine grating with high efficiency.

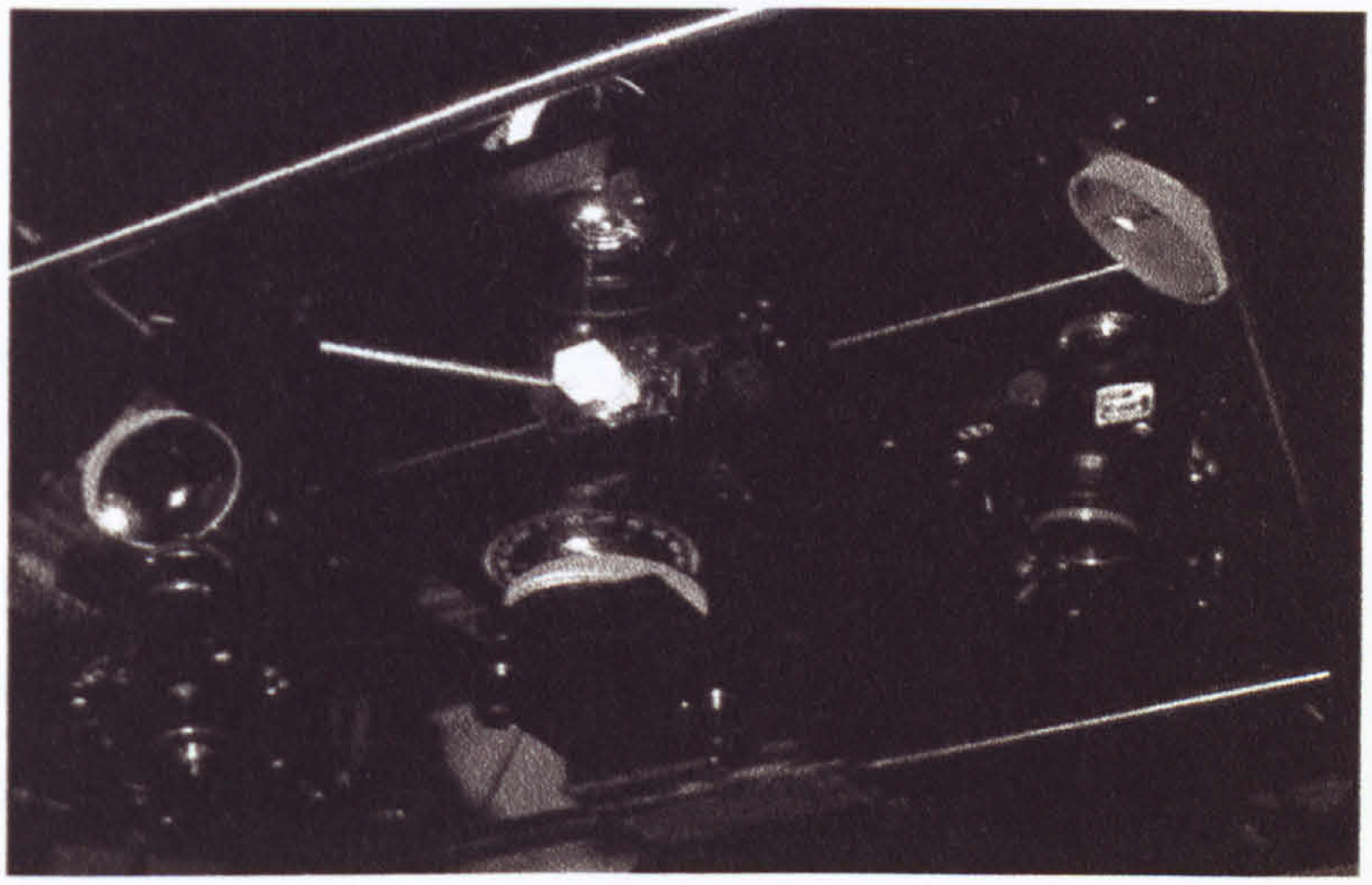


Fig. 8. 7 Example of application of symmetrical beam splitting device

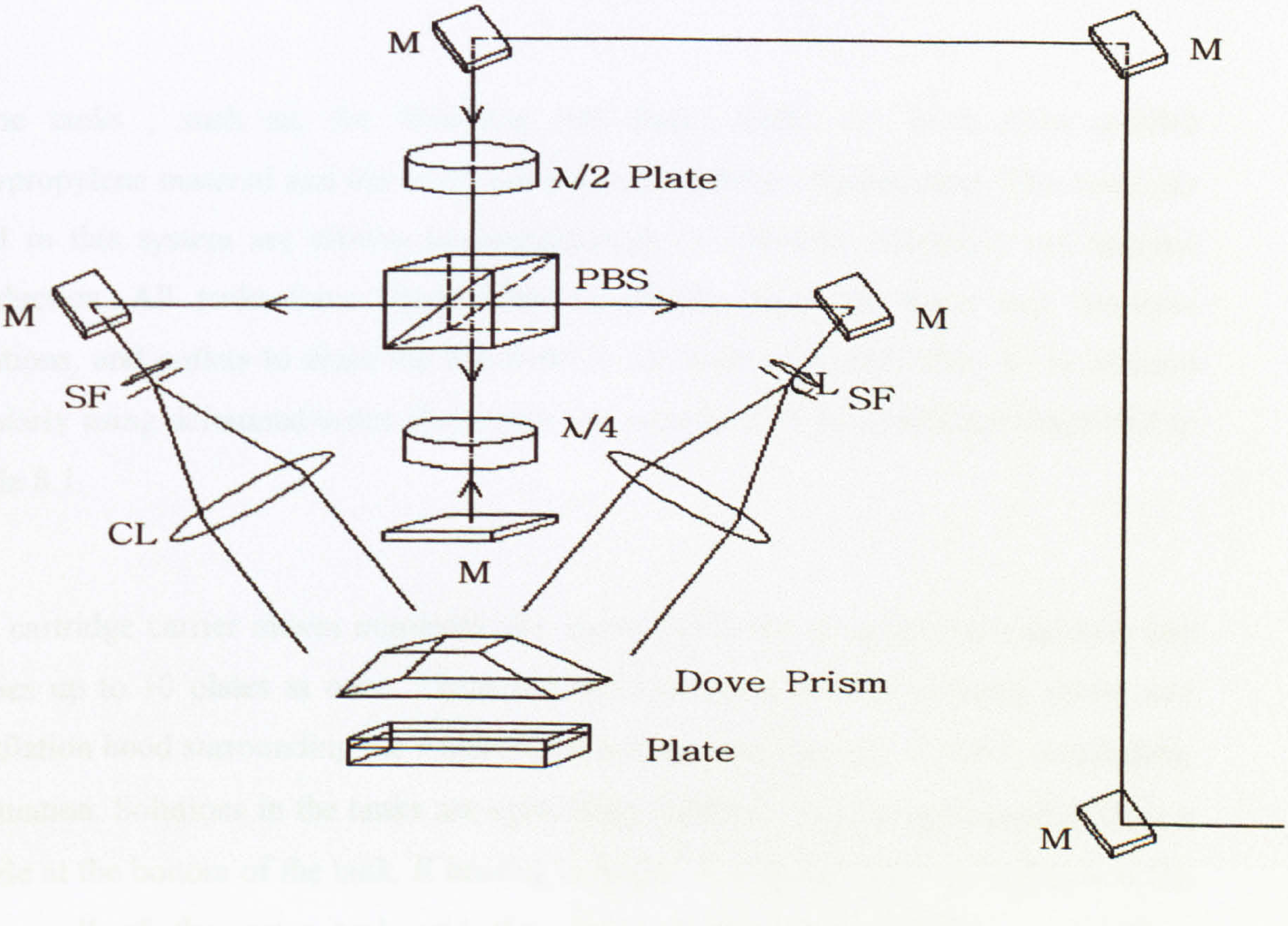


Fig. 8. 8 The diagram of recording system using symmetrical beam splitting device

8.2 Apparatus for SHSG Processing

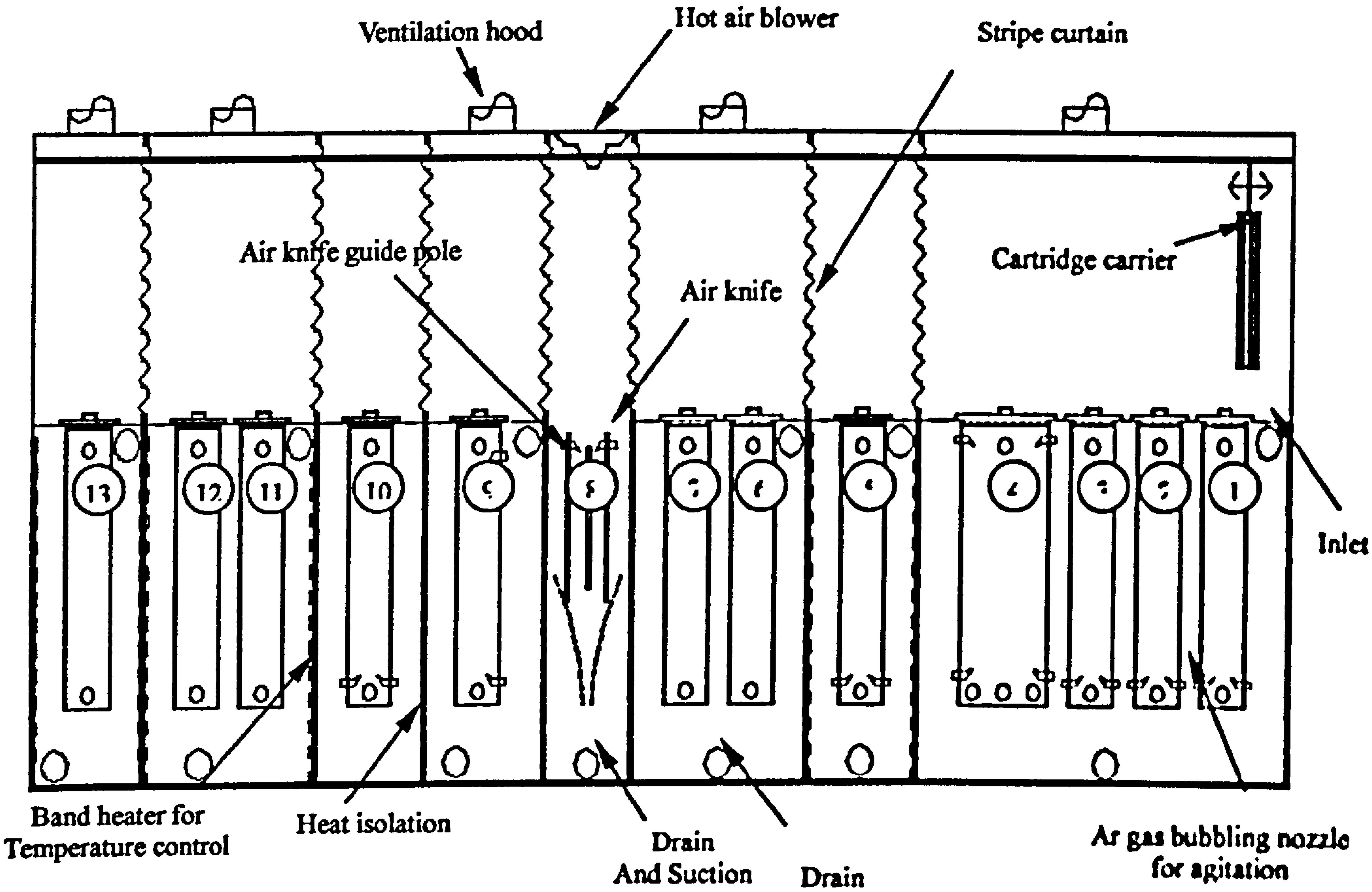
8.2.1 Wet Processing Machine

Most of this work has been devoted to the development of silver halide material processing. The process has been done manually during the earlier stage of this work since the process had to be optimized and finely tuned until the best conditions are obtain. After the optimal condition was achieved, the design of processing equipment has been considered to obtain consistency in processing and HOE quality.

The main SHSG processing steps are 9 and the processing time is quite long compared with normal silver halide processing. And HOEs have to be processed sequentially without interruption and change in environmental conditions. An enclosed system has been designed to accommodate these conditions. The outline of the system is shown in Fig. 8.9. This system is composed of 12 baths and one drying chamber, which are described in Table 8.1 briefly.

Some tanks , such as, the bleaching and fixing baths are made from welded polypropylene material and the other tanks are made from stainless steel. The materials used in this system are chosen in consideration of chemical resistance and thermal conduction. All tanks have liquid inlets to supply deionized water and chemical solutions, and outlets to drain the solutions in the tanks. All tanks have to be cleaned regularly using deionized water. Functions and structures of each tank are illustrated in Table 8.1.

The cartridge carrier moves automatically according to the programmed sequence and carries up to 10 plates at once. There are vinyl curtains, thermal isolation plates and ventilation hood surrounding the tanks to control the humidity and to avoid temperature fluctuation. Solutions in the tanks are agitated by bubbles of argon gas supplied from a nozzle at the bottom of the tank. If heating is required, a band heater is employed at the inner wall of the outer tank and the temperature is controlled by a feedback thermocouple located inside and outside the tank.



(1) Prehardening (with Ar gas bubbling method)
(2) Developing (with Ar gas bubbling method)
(3) Bleaching (with Ar gas bubbling method)
(4) Washing (with N_2 gas bubbling, DI water shower and quick drain)
(5) Washing in hot water (with heater)
(6) Intermediate dehydration (50:50; water: solvent, with heater)
(7) Intermediate dehydration (80 solvent, with heater)
(8) Drying (with air knife, hot air blower, wall preventing water spattering and air suction hole at the bottom)
(9) Intermediate vapour hardening (with heater, ventilation and vapour supplier)
(10) Fixing (with Ar gas bubbling method)
(11) Dehydration (50:50; water: solvent, with heater)
(12) Dehydration (100% solvent, with heater)
(13) Dehydration (100% boiling solvent, with heater)

All tanks have a refilling and drain system to clean inside of the tank and to supply fresh solution.

Fig. 8. 9 Outline (schematic diagram) of the SHSG processing system

Table 8. 1 Constitutions of SHSG processing system

Step	Function (solution|)	Constitution
Preharding	- Preharden AgHal emulsion - Hardening agent (*Formalin)*	- Ar gas agitation (4 bubble nozzles) - Stainless steel
Developing	- Developing exposed plate - Developer (G282c)	- Ar gas agitation (*4 bubble nozzles)* - Stainless steel -
Bleaching	- Bleaching developed plate - Rehalogenating bleach	- Ar agitation (4 bubble nozzles) - Polypropylene
Washing	- Wash and rinse processed plate - Deionized water - Nitrogen gas	- Shower nozzle (16 nozzles shower nozzle) - N2 bubble (bubbling plate at bottom) - Quick drain - DI Water supply
Fixing	- Fix bleached plate - Swelling-free fixer	- Ar agitation (4 bubble nozzles) - Polypropylene
Hot washing	- Enhance hardening - Heat treatment - Deionized water -	- Ar agitation (4 bubble nozzles) - Band heater - Stainless steel
Intermediate dehydration	- Dehydrating - Ethanol mixture	- Stainless - Two step dehydration
Drying	- Remove water on the surface - Nitrogen gas - Hot air	- Long linear nozzle (35 cm long) - Spatter prevention - Stainless steel
Vapour hardening	- Surface hardening - Heat treatment - Vapour hardening agent	- Vapour supply system - Band heater
Dehydration	- Final dehydration - Isopropanol	- Stainless steel - Three step dehydration
Cartridge moving	- Programmed moving - Up & down capable	- Moving part (stain steel) - Cartridge (Teflon)

8.2.2 Vapour Hardening System

As described briefly in the previous paragraph, a vapour-hardening tank has been designed to harden the surface of the emulsion in vapour. Surface hardening is very important in SHSG processing since microvoids located near the surface may very easily burst during the final dehydration step.

Several methods and types of equipment have been investigated to obtain optimal conditions for surface hardening. Initially, a spin coating and baking process was considered because it is very common process for the purpose of coating liquid materials on a substrate. Generally, drying of coated materials and solvent vapourization take place during spinning and baking. Normally baking is performed in an oven or on a hot plate. Alternatively, a convection microwave oven may be used. After the spin coating step, uneven fringes are found on the emulsion surface caused by the friction of liquid material with air during the spinning. Thus encapsulated spin coater which minimize the air-friction should be used for this application. Other method for a coating hardener may be roll coating, which is equally good as spin coating. The results done by these methods seemed to be good, but have to be investigated more carefully in the near future.

Hardening in the vapour hardener is preferred because it is a non-wetting process. The vapour hardening system is designed as in Fig. 8.10. Vapour is supplied through the nozzles from an outside-located container by boiling. A small pump is employed at the vapour inlet to adjust the pressure of the vapour in the container. The pressure is controlled by the pump and a pressure gauge. Normally, a pressure value from 1.1 to 1.5 atm has been used in this work. Heat treatment is also important to enhance the hardening process in the emulsion. Therefore heating by hot circulating water has been used in this system. The emulsion contains moisture after vapour hardening because the hardener is an aqueous solution. Hence the vapour-hardened emulsion need to be brought to a drying bath (Fig. 8.9, (8)) to remove the moisture.

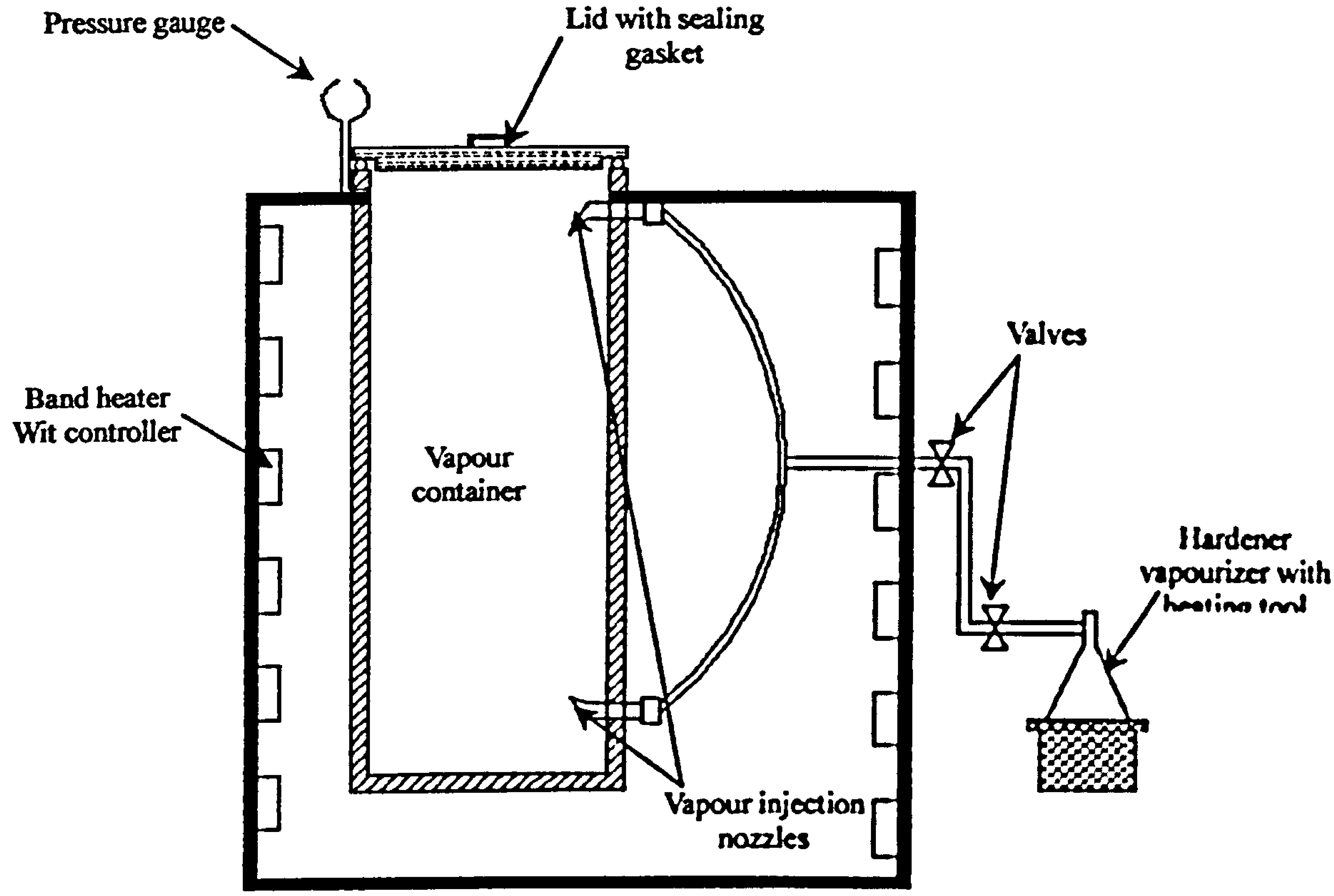


Fig. 8. 10 Schematic diagram of vapour hardening system

The equipments and apparatus mentioned in this chapter have been used to produce large-scale HOEs such as diffusers and extreme angle recorded reflector. The consistency and reproducibility were good enough to be applied to mass production.

Chapter 9

Conclusions and Direction for Further Research

9.1 General Conclusions

This work has been performed primarily with an aim to develop HOEs (holographic optical elements) applied in modern display systems. The most important requirements for the display devices are high light efficiency, full colour representation and low noise. Thus HOEs for the display application should possess the characteristics which satisfy these requirements.

Although existing holographic recording materials and processing methods have their own merits, they have drawbacks as well. In this work, I have surveyed the state of the art of the holographic recording materials and the history of the SHSG (silver halide sensitized gelatin) process. I found that a new scheme for holographic processing is necessary to overcome the drawbacks of existing materials and processing methods. As a result, I have concluded that the SHSG method might be the most appropriate candidate.

The various processing methods for the SHSG holograms are investigated comprehensively. The influence of hardening on the microvoid-structure, the wet-processing steps and the dehydration process has been examined. Particularly, the importance of hardness and the hardening procedure before, during and after process have been emphasized. A new SHSG process for transmission HOEs have been derived, which can be adapted to different holographic plates. The results of the transmission SHSG were rather good and the efficiency was higher than 95%. The new SHSG process has been found to be suitable for the manufacturing of high-quality, high-efficiency HOEs of transmission type.

The SHSG process applied to reflection HOEs is more difficult to carry out than that of transmission HOEs because of the differences in structure and density of fringes formed during recording and processing. By better understanding the hardening characteristics of gelatin and its role in SHSG processing, a process for AgHal emulsions with ultra-fine-grains has been found. The effect of selective hardening has been investigated to find the optimum hardening condition for the SHSG process. The new SHSG processing of Slavich AgHal emulsions is appropriate not only for reflection HOEs but also transmission HOEs. The characteristics of HOEs processed with the new SHSG method are outstanding. The reflection SHSG HOE exhibited up to 96% diffraction efficiency. A variety of optical elements can be manufactured since the Slavich materials have relatively high sensitivity compared with DCG and photopolymer materials. Using the new SHSG process, colour HOEs as well as colour display holograms with high quality can be produced. Unfortunately however, because of the poor quality of AgHal emulsions recently produced by Slavich, it was not possible to obtain colour HOE samples of the quality expected until a appropriate panchromatic emulsion can be obtained.

The capability of the new SHSG process has been tested by the development of HOEs for display applications. The SHSG method has been applied firstly to the replication of diffusers to improve the brightness and viewing angle of LCDs. The copied diffusers processed with the new SHSG method had both volumetric and surface relief effect. The microscopic structure of the copied diffuser was investigated using SEM (scanning electron microscopy) to confirm these effects. The characteristics of copied diffusers were exceptional in terms of transmittance and diffusing angle.

Additionally, some other HOEs for display application, such as, extreme angle recorded HOEs for backlight systems and multiply stacked holographic reflectors for reflective LCDs, have been examined and evaluated. I have reviewed problems in edge-lit and extreme angle recording and investigated new approaches to solve those problems. The new recording methods and apparatus such as cocktail of index-matching fluid, illumination by sheet beam, specially designed fluid tank and LED light source have been applied to develop the backlight device for the LCDs.

An innovative idea of a multiply stacked pixellated reflector for the reflective LCD has been proposed and investigated. I have been examined the feasibility of recording pixellated HOEs using newly designed dual mask aligner. The preliminary test of the idea has been performed but has not been completed yet. The stacked holographic reflectors and extreme angle recorded HOEs can improve the quality of LCDs and can make the structure of the LCD device simpler.

Various apparatus and equipments have been developed throughout this research work related to the process of HOEs and the applications of the SHSG process.

The quality of both transmission and reflection HOEs processed with the new SHSG method developed in this work, are so good that these processing methods can be applied to the manufacturing of HOEs, not only for display devices, but also for applications in other modern optical systems. The new SHSG method developed in this work can open up new fields of HOE applications. HOEs designed in this work may give an opportunity to make technical breakthrough in the field of flat panel displays.

9.2 Direction of Future Research

Further research on the SHSG process will be carried out to make improvements and to more precisely evaluate the characteristics such as scattering and reliability. Another task to be performed in the near future is to find a new type of AgHal emulsion which is suitable for colour HOEs recorded in a single emulsion. Moreover new designs and manufacturing of the SHSG processed HOEs will follow as a result of improved AgHal emulsions.

There may be plenty of potential applications of the new SHSG process. First of all, the ultra-high-resolution AgHal materials combined with the SHSG processing are suitable for many types of display holograms. For example, the original masters for embossed holograms can be recorded with this technique as well as masters for contact copying into photopolymer materials, including also full colour masters. Employing the new SHSG technique a variety of HOEs can be manufactured which includes also relatively large elements. Since some of the AgHal materials are panchromatic, it is relatively easy to record colour HOEs, e.g., bright white volume holographic reflectors for LCD screens as well as colour HUD's. Devices for edge-lit holograms are another potential application.

Since AgHal materials can be made infrared (IR) sensitive, it is possible to make efficient IR HOEs in this part of the spectrum. These methods need to be further investigated applying the new SHSG processing technique. Holography has been recognized as a technique for optical interconnects. Applying the new SHSG technique in this field may result in an improved quality of the components. The potential of recording such devices in infrared (e.g. at 1.06 μm) may become very attractive in the future.

The distribution and size of microvoids formed by the SHSG processing is very uniform and controllable. The SHSG processing is a new way to produce uniform porous materials. If it is possible to fill the microvoids with other materials such as liquid crystal, various polymers and band gap materials, completely different devices can be produced. As an example, if microvoids are filled with liquid crystal, the device acts similarly to the PDLC that has been described in section 5.3.1. The similarity is based on the driving method of liquid crystal but the characteristic of the PDLC is not comparable with a microvoid-filled device because the droplet size differs by an order of magnitude. The size of droplets in PDLC is in the order of several micrometers to several tens of micrometers but for the microvoids-filled device it is in the order of several tens of nanometers to several micrometers. The droplet size in those devices affects driving voltage, brightness and contrast ratio of LCD displays.